# Defect dynamics in MAPbI<sub>3</sub> polycrystalline films: the trapping effect of grain boundaries.

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Metal halide perovskites of composition ABX<sub>3</sub> (A=CH<sub>3</sub>NH<sub>3</sub>\*, Cs<sup>+</sup>, ...; B=Pb<sup>2+</sup>, Sn<sup>2+</sup>; X=I<sup>-</sup>, Br<sup>-</sup>), have attracted great interest as the most promising class of materials for low-cost photovoltaics with over 25% certified power conversion efficiency. An important aspect for their efficiency, e.g. for improving the open circuit voltage, and stability is the formation and dynamics of point defects, e.g. vacancy and interstitials of the various chemical species. In particular, recently it has been shown that defects strongly interact with grain boundaries, which, for example, prevents a quick restoration of the film under dark conditions [Phung et al., Adv. Ener. Mat., accepted for publication]. In this article we make use of molecular dynamics to compute the dynamics and energetics of a iodide vacancy,  $V_I^{\bullet}$ , and Interstitial,  $i'_I$ , interacting with  $\Sigma 5/(102)$  grain boundaries at finite temperature. We show that the polarization

charge of grain boundary drives the dynamics of charged defects,  $V_I^{\bullet}$  and  $i_I^{'}$ . A type of grain boundary can have different kind of terminations; in particular  $\Sigma 5/(102)$  has two types of termination of opposite polarization attracting defects of opposite charge. The long-range interaction of grain boundaries with point defects might help splitting Frenkel pairs formed in solar cells under illumination and can prevent their recombination in dark conditions.

Keywords: point defects • grain boundaries • metal halide perovskites • molecular dynamics

#### Introduction

From the original work of Miyasaka and coworkers [1], (Hybrid organic-inorganic) metal halide perovskite (MHP) based solar cells have made an impressive progress, reaching a maximum power conversion efficiency (PCE) exceeding 25% (25.2%), higher than well-established materials such as multi-crystalline silicon (23.3%) and very close to the single crystal counterpart (26.1%) [2]. Applications of MHP is not limited to single junction solar cells; thanks to their tunable bandgap, efficient narrowband emission, high photoluminescence quantum yield, and short radiative lifetime MHP are being considered for fabricating emitting diodes [3-7], lasing [8-11], photodetectors [12,13], color conversion for light-based communications and illumination [14], field effect transistors [15] and large-bandgap component for tandem solar cells [16].

MHPs have an ABX<sub>3</sub> formula, where A<sup>+</sup> is a monovalent cation, which can be either organic (e.g. methylammonium, MA<sup>+</sup>) or inorganic (e.g., Cs<sup>+</sup>), B<sup>2+</sup> is a divalent cation, typically Pb<sup>2+</sup> or Sn<sup>2+</sup>, and X<sup>-</sup> is an halide, I<sup>-</sup> or Br<sup>-</sup> or a mixture, depending on the application. Each of these chemical species can form the corresponding kind of point defects, e.g. vacancy or interstitial. These defects, and their migration, were found to be responsible for J-V hysteresis [17-19] and reversible and irreversible degradation of perovskite solar cells [20]. Recent photoluminescence (PL) and PL microscopy experiments have shown that light can induce the formation of defects, probably Frenkel pairs of iodide and MA ions, which migrates toward grain boundaries[21]. Upon cessation of illumination the film tends to restore its initial structure, with complementary defect recombining. However, the rate of relaxation to the original structure depends on the characteristics of the sample: single crystals and films with larger grains relax faster than films with smaller grains. This has been explained in terms of a possible trapping mechanisms of point defects by grain boundaries, which has been confirmed by atomistic simulations.

In this work we investigate in detail the role of grain boundaries in attracting and, possibly, trapping defects, the relation between their characteristics and properties concerning interaction with vacancies and interstitials. To this aim, we make use of molecular dynamics simulations using the MYP potential <sup>-</sup> to compute the dynamics and energetics of a iodide vacancy,  $V_I^*$ , and Interstitial,  $i'_I$ , interacting with  $\Sigma 5/(102)$  grain boundaries, a prototypical grain boundary in MAPbl<sub>3</sub>. Anticipating our results, we show that charge polarization of grain boundary is the main responsible for the attraction of  $V_I^*$  and  $i'_I$ , and that different kinds of terminations of the  $\Sigma 5/(102)$  grain boundary have opposite polarization, thus attract defects of opposite charge. We conclude that the long-range attraction of grain boundaries for defects might help splitting Frenkel pairs and can prevent their quick recombination upon cessation of illumination.

# **Results and Discussion**

The atomistic model here adopted to study the interaction between point defects and grain boundaries consists of two crystal grains with planar Σ5/(102)

boundaries (see Figure 1);  $\Sigma 5/(102)$  is a prototypical boundary in MAPbl<sub>3</sub> forming along the (102) crystallographic plane with 53.1° tilt angle [24]. Each grain presents two terminations, a Pbl<sub>2</sub>-termination (left) and MAI-termination (right). The system is periodically repeated, thus the sample features two interfaces corresponding to terminations of opposite kind, which gives us the chance to study the effect of each specific termination on the trapping of different defects. Each grain has an *in-plane* size of 20 stoichiometric units, corresponding approximately to 13 nm. The system is evolved according to the MYP force field (Model potential for hYbrid Perovskites) developed by Mattoni et al. [22,23,25], which has been successfully applied to study diffusion of point-defects in the bulk [26], at surfaces [27-29] and the dielectric response to electric fields [30]. Computational details are provided in the **Experimental Section**.



**Figure 1.** a) Finite temperature trajectory of a iodide vacancy initially formed at the center of the crystalline grain **G1**.  $V_1^*$  migrates toward the MAI-terminated grain boundary; once it reaches the grain boundary,  $V_1^*$  moves tangentially to it. b) (102) slab of MaPbl<sub>3</sub> illustrating the ideal Pbl<sub>2</sub> and MAI terminations. c) energy profile of a iodide vacancy as a function of the position of  $V_1^*$  in the grain. The energy profile is obtained by removing a  $\Gamma$  ion from the sample at different positions and then relaxing the structure (points). The. The interpolated profile (solid line) presents two energy minima, an absolute minimum at the MAI-terminated boundary and a local minimum at the Pbl<sub>2</sub>- one.

A first interesting remark concerns the structure of the grain boundaries. In previous DFT simulations [24,31], grain boundaries were simulated with crystal grains of maximum 5 stoichiometric units; the initial structure was either optimized [31] or evolved at 300 K for a short time (4 ps) [24]. In both cases the grain boundary structure strongly resembled the (initial) ideal one: indeed, local optimization or short simulation times prevent a proper exploration of the possible atomistic configuration of grain boundaries. This is especially important if one considers that, to achieve a complete relaxation of the grain boundary structure, significant rearrangements are needed, which typically requires to overcome (free) energy barriers to which is associated a transition time largely exceeding the timescale achievable by DFT simulations [32-34]. **Figure 1a** shows the structure of the Pbl<sub>2</sub>- (blue) and MAI- (red) terminated grain boundaries. We remark that here we denominate Pbl<sub>2</sub>- and MAI-terminated planar  $\Sigma 5/(102)$  boundaries only with reference to the chemical species present in the outmost layer of the grain. This is better illustrated with reference to a (102) of MAPbl<sub>3</sub>, shown in **Figure 1b**. One notices that while the Pbl<sub>2</sub>-terminated grain boundary is relatively sharp, resembling the regular structures obtained in the *ab initio* simulations, the complementary grain boundary, probably due to the softer MAI termination, presents bigger distortions of the local structure. Indeed, the first 1-2 layers across the grains are rather amorphous-like. Classical MD, though driven by less accurate forces, allows to simulate the system for nanoseconds, even tens or hundreds of nanoseconds, if necessary. This allows the system to extensively explore the configuration space and identify the more complex structure of the MAI-terminated grain boundary. Of course, because of the lower accuracy of classical MD, one should focus on qualitative rather than quantitative aspects of results.

We now investigate the effect of grain boundaries on the dynamics of defects, in particular of a iodide vacancy,  $V_1^{\bullet}$ . A  $V_1^{\bullet}$  is created in the middle of one of the grains (**G1**) and it is left to evolve at 400 K temperature for 0.5 ns. We choose this temperature due to higher diffusivity of ions at higher temperatures. Note that the diffusion mechanism is unchanged between 400 and 300 K [26], whereas higher temperature shorten the simulation time. After an initial random wandering, the vacancy starts to drift toward one of the two grain boundaries, namely the MAI-terminated grain boundary (**Figure 1a**). Once the gain boundary is reached the vacancy moves only along the interface between the two grains: atomic displacements are observed only tangentially to the grain boundary. To understand the origin of the complex vacancy dynamics we computed its energy profile, i.e. the energy of a system containing a iodide vacancy as a function of its position. The energy profile, shown in **Figure 1b**, consists of different domains. A central domain, far from both grain boundaries, in which the energy profile is relatively flat, with a gentle slope in the direction of the MAI-terminated grain boundary. At a distance of 2-3 nm from the grain boundaries a stronger attractive (MAI-terminated) or repulsive (PbI<sub>2</sub>-terminated) force acts on the vacancy, which produces the quick drift of  $V_1^{\bullet}$  toward the MAI-terminated grain boundary. Finally, very close to both grain boundaries the energy profile is parabolic-like: regardless the type of termination they are both attractive to  $V_1^{\bullet}$ . It is worth remarking that the domains are identified in both grains present in the computational sample but, though qualitatively similar, the energetics between the two grains show some quantitative difference on which we will come back in the following.

Let us focus first on the grain denominated **G1** (Figure 1 and 2). The MAI-terminated grain boundary is an absolute minimum of the energy and to reach the bulk of the grain a vacancy trapped here must walk 0.5 eV up in energy. On the contrary, the PbI<sub>2</sub>-terminated grain boundary is a local minimum and once overcome the 0.5 eV barrier, a  $V_1^*$  can reach the bulk of the grain going down in energy. Despite their 1.5 eV energy difference, both grain boundaries can trap iodide vacancies. Similarly, also in the case of grain **G2** both boundaries are attractive to  $V_1^*$ ; also in this case, PbI<sub>2</sub>- and MAI- terminations are local and global energy minima of a iodide vacancy, respectively. However, at a variance with **G1**, in **G2** the absolute minimum is deeper, the energy of an iodide vacancy at the MAI-terminated boundary of **G2** is ~1.2 eV lower than in the bulk of the grain, against ~0.5 eV for **G1**. These values of the energetics of  $V_1^*$  in **G1** and **G2**, relative energies of the various grain domains and migration energy barriers, is well above the limit of accuracy of the MYP model, which can be estimated to be ~0.1-0.2 eV (compare, e.g., vacancy formation and migration energies calculated by present force field [26] to the corresponding *ab initio* data [35]). This makes us confident that present results are qualitatively accurate and will be used in the following to interpret experimental results [21].

It is interesting to identify the structural characteristics determining the attraction of a vacancy for a grain boundary of a given termination, why  $V_l^*$  is attracted by MAI-terminated grain boundaries rather than PbI<sub>2</sub>-terminated ones. One can identify two reasons for this: either i) the charge polarization of

grain boundaries, i.e. a change imbalance producing an electric field attracting/repelling changed defects, or ii) structural distortions, which might make less or more expensive host a vacancy in a zone with a higher or lower crystal deformations. Of course, the two effects can be combined, producing a cumulative attraction/repulsion. Recently, Caddeo et al. [27] have shown that (001) MAPbI3 surfaces can attract and trap suitably charged defects due to both polarization charge density at the surfaces and structural effects. Thus, here we first investigate the charge density as a function of the position along the slab,  $\rho_{\rho}$  (Figure 2), and then consider structural distortions. One notices that within the grains the charge density oscillates around zero, with fluctuations depending on the discretization of the space used to compute  $\rho_e$ . In correspondence of the grain boundaries one observes larger fluctuations of the charge density, positive at the Pbl2-terminated boundary and negative at the MAI- one. The polarization charge at the grain boundaries is consistent with the polar nature of hybrid perovskites and supported by ab initio results for a (102) MaPbI3 slab (Figure SI1), showing that also in this case the MAItermination is attractive for  $V_I^{\bullet}$ . Polarization charge of Pbl2- and MAI-terminated grain boundaries might explain the trajectory of  $V_I^{\bullet}$ , which moves consistently with the electric field  $\vec{E}$  generated within the grains by the polarization charge at the two ends. Indeed, the two grain boundary terminations behave like the plates of a planar capacitor. The effective electric field acting on the charged defects depends on the dielectric polarization  $\varepsilon$  of the bulk of the crystalline grain. The dielectric function of MAPbI3 is mainly ionic, thus we expect that  $\varepsilon$  is well represented by the MYP force field. This has been confirmed in a recent work [30], where it was found that the main qualitative features of the MAPbI3 dielectric function (e.g. the temperature and frequency dependence) are reproduced by the present force field. In the following we will analyze the polarization of MAPbI3 grains in detail. Summarizing, we expect that the energetics and dynamics of charged defects within MAPbI3 grain identified in our simulations is a good representation of the behavior of real materials



Figure 2. Charge density  $\rho_e$  along the sample. One notices that the within the grains the density oscillates around zero, with an amplitude that depends on the size of the binning used to discretize the x axis. At the grain boundaries the charge density has a large fluctuation, positive and negative at the Pbl<sub>2</sub>- and MAI-terminated boundary, respectively.

From Figure 1 (panel c) one notices that the shape of the vacancy potential is more complex than the linear profile of planar capacitor, and, furthermore, the energetics of  $V_I^*$  in the two grains is different from each other, deviating from the ideal capacitor case. This suggests that there might be an interplay between the effect of polarization and structural grain boundary related distortions on the energetics of  $V_I^*$ . A similar interplay has been recently observed for defects within a 001 crystalline slabs [27].

To gain physical insight in the ionic response within the crystal grains we consider two observables that have frequently been reported in the literature to characterize the structure of halide perovskites and which affect their energetics: the tilting angle, the rotation of the Pbl<sub>6</sub> octahedra around their I-Pb-I axes with respect the ideal cubic orientation, and the Pb off centering, how much Pb lies outside the center of the octahedron formed by the corresponding six iodide ions (see inset in **Figure 3**). In principle, another important structural characteristic is the Pb-I bond-length but previous *ab initio* studies have shown that this parameter has minimal variation upon structural (orthorhombic, tetragonal, cubic) or even chemical composition modifications [36-38]. Halide perovskite structures are distinguished by their tiling angles; orthorhombic, tetragonal and cubic structures have three, one and zero non vanishing tilting angles and one observes genuine first (orthorhombic-to-tetragonal) and second order (tetragonal-to-cubic) phase transitions at increasing temperature. Moreover, by experiments and simulations It was shown that Pb off centering [39] and tilting angle [36,37,40] affect the bandgap; namely, an increase of the distortion of the structure brings to a reduction of the energy of the valence band due to the reduction of the (unusual) antibonding overlap between Pb 6s and I 5p atomic orbitals. These observations bring to the conclusion that structural distortions are relevant for the study of the energetics of the bulk and of the embedded point defects as well.

In **Figure 3** we report the average value of the Pb off-centering  $r_{off}$  (a) and Pb-I-Pb angle  $\alpha$  (b).  $\alpha$  is used as a convenient proxy of the tilting angle [41]. Pb off-centering is here defined as the difference of the positions of a Pb<sup>2+</sup> ion from the barycenter of the six I<sup>-</sup> ions forming the corresponding octahedron. We stress that these values have been averaged over the entire simulations; instantaneous values can be significantly different from the average ones. As

a first remark, one observes that in correspondence of the grain boundary both  $\alpha$  and  $r_{off}$  diverge from the bulk value. This is not surprising as at the grain boundary the structure is highly distorted. At a distance of 1-2 nm from the nominal center of a grain boundary both  $\alpha$  and  $r_{off}$  recover the characteristic value of bulk perovskite, though  $r_{off}$  is slightly higher in **G2** than in **G1**. However, there is no evident trend of the tilting angle or off-centering as a function of the distance from the grain boundary which might be responsible for a different energetics of  $V_I^{\bullet}$  as a function of its position. Thus, if structural distortions play any role il the bulk of the grains it must be of different kind.

The Pb off-centering is a vector quantity that requires the calculation of its three cartesian components. In **Figure 3c** we show the values of  $r_{off} - r_x$  (red),  $r_y$  (blue) and  $r_z$  (black) - as a function of the position along the computational sample. One notices that  $r_z$  oscillates around zero all along the sample.  $r_y$  has a similar behavior, apart i) a gentle slope toward the MAI termination in both grains and ii) a large negative peak in correspondence of the grain boundaries. At a variance with the other two,  $r_x$  has large negative and positive values all over **G1** and **G2**, respectively. In correspondence of the grain boundaries one observes large positive and negative fluctuations. By recalling that to a displacement of Pb<sup>2+</sup> out of the barycenter of 1<sup>-</sup> ions corresponds a net electric dipole, one realizes that a non zero  $r_x$  corresponds a contribution of the inorganic framework to the dielectric induced by the net charge at the grain boundaries. This polarization mechanism is visually shown in **Figure 3e** and it is consistent with the PbI component of bulk MAPbl<sub>3</sub> polarization under electric fields[30]. In turn, this polarization, acting as a dielectric, screens the interaction between charged point-defects and the grain boundaries on  $V_1^*$ , producing an *attenuation* of the electric field attracting the positively charged defect to the MAI termination. The magnitude of the dielectric polarization, i.e. the absolute value of  $r_x$ , is higher in **G2** than **G1**. Thus, the screening – dielectric constant – is larger in **G2** than in **G1** and the electric field acting on  $V_1^*$  is smaller in **G2** than **G1**.



**Figure 3.** Distortions of the inorganic Pbl<sub>3</sub> framework and orientation of MA<sup>+</sup> ions in MAPbl<sub>3</sub> grains of the computational sample. At the top of the figure are reported two cartoons illustrating the off-centering and tilting. In panels a) and b) are respectively reported the values of the Pb off-centering out of the barycenter of the corresponding octahedron formed by I<sup>-</sup> ions,  $r_{off}$ , and Pb-I-Pb angle,  $\alpha$ , measuring the tilting of the octahedra. In panel c) are reported the x, y and z components of  $r_{off}$ . In the inset is shown a magnification of  $r_y$  to show that though smaller in magnitude, also the y component of  $r_{off}$  has a non-trivial shape. Panel d) reports the x, y and z components of the dipole associated to the organic cation MA<sup>+</sup>. Panel e) visually illustrates the polarization of **G1** and **G2**. Red and blue spheres centered at the Pb sites of the inorganic frameworks represent the Pb<sup>2+</sup> positions, center of the positive charge, respectively. To make the polarization associated to Pb off-centering more evident  $r_{off}$  has been magnified by a factor 2.5. Red and blue spheres centered at MA<sup>+</sup> positions correspond to N and C positions, respectively. Ab initio calculations [42] have shown that the MA<sup>+</sup> dipole has a consistent orientation.

On top of Pb off-centering, also the orientation of the dipolar organic cation MA+, of dipole moment  $\mu = 2.3D$  [43], possibly contribute to the dielectric polarization of the grains. Indeed, orientation of MA+ gives the major contribution to ionic dielectric polarization of bulk MAPbI3 [30]. **Figure 3d** shows the three components of the N-C vector  $\tau$ :  $\tau_x$ ,  $\tau_y$  and  $\tau_z$ . Like in the case of  $r_{off}$  and  $\alpha$ ,  $\tau$  is the average value of the orientation of MA+ over the entire simulation: methylammonium rotates almost freely within the inorganic framework but it spends more time along specific directions. Like in the case of  $r_{off}$ , also  $\tau$  is oriented consistently with  $\vec{E}$ ; thus, consistently with bulk MAPbI<sub>3</sub>, MA<sup>+</sup> orientation polarization contributes to screening the effect of electric

field associated to grain boundaries on  $V_i^{-}$ . At a variance with Pb off-centering,  $\tau_x$  does not show any appreciable difference in absolute value between **G1** and **G2**; thus, MA<sup>+</sup> orientation gives an equivalent contribution to the screening of attractive forces acting on charged point defects in **G1** and **G2**.



Figure 4. path of an interstitial iodide initially formed at the center of the crystalline grain G2.  $i_I$  migrates toward the Pbl<sub>2</sub>-terminated grain boundary, i.e. in the opposite direction of  $V_I^*$ 

To validate the idea that charged point defects migrate to grain boundaries mainly driven by charge polarization at the interface between different crystallites, we followed the dynamics of a iodide interstitial,  $i_{I}$ , created at the center of **G2** (Figure 4). Consistently with the hypothesis discussed above,  $i_{I}$  migrates toward the Pbl<sub>2</sub> termination, i.e. in the opposite direction of  $V_{I}^{\bullet}$ .

Present results allow us to formulate a possible explanation for recent results from Pungh et al.[21], who have shown that iodide and, possibly, methylammonium Frenkel pairs formed upon intense illumination migrate out of the focus of a laser. Upon cessation of illumination, defects recombine but recombination is faster in monocrystals or in polycrystalline samples with larger grains with respect to films with smaller crystallites. Grain boundaries help separating defects of opposite charge, which prevent their quick recombination and allow to achieve high off-equilibrium concentrations possibly affecting the optical characteristics of MAPbI3. Of course, charged defects attracted by grain boundaries of opposite sign results in a reduction of the charge polarization of the latter and, hence, a reduction of their attractive force [27]. This makes the Frenkel pair splitting less efficient, thus increasing defects recombination. This mechanism might prevent a complete degradation of MAPbI3 under (moderate) illuminations. Once illumination is ceased the system tends to restore the equilibrium defect concentration by recombination of complementary defects. However, since defects are trapped at different grain boundary recombination kinetics is determined by the detrapping of defects and, in turn, detrapping time depends exponentially on the height of the barrier the defects have to overcome [32,34,44], the process is slower in systems presenting a higher concentration of grain boundaries, such polycrystalline films with small grains. As a consequence, defects recovery is slower in small grains systems. We also expect that the mechanism of separation and trapping/detrapping of defects at the grain boundaries (or surfaces or interfaces) contribute to explain the slow current transients, memory effects and hysteresis [27,35,45]1 observed in hybrid perovskites.

## Conclusions

In this work we performed finite temperature molecular dynamics simulations aimed at investigating the interaction between grain boundaries and halide defects, vacancies and interstitials, in MAPbl<sub>3</sub>. We considered Σ5/(102) grain boundaries of different termination and found that they are charge polarized,

with opposite polarization. This polarization charge density at the boundaries produces electric field driving  $V_i^{-}$  and  $i_i^{-}$  at opposite terminations, thus separating Frenkel pairs that might be formed by the action of external stimuli, e.g. illumination. The electric field induced by grain boundaries results also in an ionic polarization of the inorganic sublattice as well as of the orientation of organic cations; this dielectric response, consistent with the bulk dielectric properties, modulates the attracting force of defects at grain boundaries, together with the structural features (e.g. strain) associated to actual of the microstructure.

Present results can explain the trapping of defects at grain boundaries observed in recent experiments and the slow relaxation to the equilibrium of films exposed to intense illumination: complementary defects are trapped at different grain boundaries and before they can annihilate they must detrap, migrate out of the basin of attraction of grain boundaries, encounter the other element of the Frenkel pair and recombine.

## **Experimental Section**

#### Classical Molecular Dynamics (MD):

The model polycrystalline film containing two  $\Sigma5/102$  twin boundaries was obtained by: (i) cutting an orthorhombic crystal of MAPbI3 with (102) surfaces; (ii) generating a replica by a mirror-symmetry about one of the surfaces; (iii) merging the two crystals after a relative shift aimed at optimal match of atoms at the boundary; (iv) applying periodic boundary conditions. The 4032-atoms model obtained by this procedure was first optimized by conjugate gradient forces minimization, then heated to 300 K or 400 K and annealed for 0.3 ns. A vacancy was generated in the central part of **G1** by removal of one iodine atom and its trajectory during the evolution tracked by calculating atomic coordination of Pb atoms. The vacancy trajectory and diffusion was studied during 0.5 ns NPT dynamics at 400 K and 1bar. Similarly, to investigate the dynamics of the interstitial defect a  $i'_1$  was created at the center of G2 by adding a iodide ion and moving another I<sup>-</sup> already present in the lattice so to form a geminal pair, which *ab initio* calculations have shown to be the equilibrium structure of this kind of defect. Also the trajectory of  $i'_1$  was tracked by identifying the position of overcoordinated lead atoms.

The energy profile of **Figure 1** was obtained by: (i) choosing an atomic configuration of the defect free model polycrystalline film equilibrated at 300 K; (ii) selecting and removing one iodine atom along a direction orthogonal to the boundaries; (iii) geometry optimization of the structure containing the defect by energy minimization; (iv) collecting all data as a function of position. The profile is obtained by a local running average over the vacancy position. All simulations were performed using the LAMMPS code [43] in combination with the MYP potential [22,23,25].

# **Supplementary Material**

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/MS-number.



**Figure SI1.** a) Image of a (102) MAPbl<sub>3</sub> slab with the Pbl<sub>2</sub>- and MAI-terminations. b) Electrostatic potential acting on a positive change. This is estimated from the sum of the socalled *bare potential, the frozen-core pseudopotential,* and the electrostatic potential determined by valence electrons:  $U_{el}(x) = U_{core}(x) + U_{valence}(x)$ . Since the  $V_l^{\bullet}$  has a positive sign, we plot  $-U_{el}(x)$ . In the main chart of panel b, and even more clearly in the zoom reported in the inset, one notices that the potential diminished going toward the MAI-termination. Thus, consistently with the classical prediction on the grain boundaries,  $V_l^{\bullet}$  is attracted at the MAI-termination.

# Acknowledgements

S. M. acknowledges PRACE for awarding him access to Marconi KNL at CINECA, Italy, through projects PROVING-IL (2019204911). A.M. acknowledges MIUR for funding the project (Grant No. 607 PON04a2 00490), M2M Netergit and PRACE for awarding him access to Marconi KNL at CINECA, Italy, through projects UNWRAP (2016153664) and DECONVOLVES (2018184466).

#### **Author Contribution Statement**

Authors contributed equally to this work.

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Formation of Frenkel pairs by illumination limits the efficiency of perovskite solar cells. We show how grain boundaries stabilize defects splitting Frenkel pairs, trapping vacancies and interstitial.