Structural Stabilities and Electronic Properties of High-Angle Grain Boundaries in Perovskite Cesium Lead Halides

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Supporting Information

ABSTRACT: Organometal trihalide perovskites are emerging as very promising photovoltaic materials, which is rivaling that of single crystal silicon solar cells despite their polycrystalline nature with relatively high density of grain boundaries (GBs). There is a lack of understanding of the effects of GBs on halide perovskites as their presence in silicon and other photovoltaic materials is generally detrimental to their photovoltaic properties. Using first-principles calculations, we systematically investigate the geometric structures of high-angle tilt GBs in halide perovskites CsPbX₃ (X = Cl, Br, and I) starting from the



coincidence site lattice model and refining using crystal shifts and lattice expansion. Electronic density of states calculations reveal that GBs in halides perovskites do not generate midgap states because of the large distance between the unsaturated atoms and the atomic reconstructions in the GB region. However, we show that the GBs can induce different very shallow states near the valence band edge that can hinder hole diffusion. We further extend the results to MAPbI₃ GBs and also show their benign effect on optoelectronic properties.

INTRODUCTION

Solution-processable organometal trihalide perovskites (OMHPs) are garnering great interest from the solar cell research community given their potential to create disruptive technology in photovoltaic industry.¹⁻³ It is quite surprising that only five years of research has enabled the power conversion efficiency (PCE) of OMHPs solar cells (PSCs) to rise from 3.8% to \sim 22%, thus rivaling that of single crystal silicon solar cells.⁴ The OMHPs have many attractive features, such as low-cost, flexibility in materials growth,⁵ as well as several unique properties including tunable band gaps and band gap alignment,⁵ strong optical absorption,^{6,7} and long-range electron-hole diffusion length of at least 100 nm.^{8,9} In parallel, all-inorganic cesium-based trihalide perovskites (CsPb X_3 , X = Cl, Br, and I) are also attracting great attention.¹⁰⁻¹⁴ Recent study showed that all-inorganic perovskites, which exhibit higher stability than the organic ones, have also huge potential in optoelectronic applications.¹⁵

Despite the extensive studies on organic and inorganic halide perovskites, most modeling studies focused on single crystalline systems although the growth of large crystals is very challenging.¹⁶ These studies elucidated many fundament properties of the halide perovskites but shed little light on effects associated with their polycrystalline nature. Most of the materials employed in PSCs are polycrystalline with grain boundary (GB) defects, which is unlikely to change in solar applications because their solution processability and cheap large-scale production is a key strength of these materials. Therefore, it is imperative to understand the impact of GBs on the performance of perovskite solar cells, which is still largely unexplored despite its importance. For example, in conventional inorganic solar absorbers, such as Si, GaAs, CIGS, CZTS, and CdTe, intrinsic GB disorders are generally considered extremely harmful to the optical performance as these create deep levels in their band gaps¹⁷⁻²¹ that act as the recombination center of charge carriers.²²⁻²⁴ To date, the major question whether GBs in PSCs help, hinder, or have no effect on the PCE has not been completely resolved. There is an increasing evidence that GBs generally degrade the PV performance and increase the hysteresis in the J-V behavior. Few studies indicated that charge recombination takes place in the GB region because of their high charge-trap densities,²⁵⁻ which can be minimized by reducing the total number of GBs.^{29,30} These findings are in conflict with a recent study by Yun et al. which argue the beneficial roles of GBs in separating charges and collecting carriers efficiently.³¹ Further, firstprinciples calculations by Yan's group suggested that GBs in MAPbI₃ do not create deep midgap states in the band structure and are thus electronically benign.^{7,21,32} Another recent study by the same group argues that the GB-induced defect state in $\Sigma 5(310)$ is close to the VBM, thus acts as a shallow trap state that can hinder the hole diffusion.³² The conflict between these

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findings underscores the complexity of these studies, and calls for more investigations to resolve many critical questions.

Modeling the GBs using first-principles methods is generally challenging because of the relatively large system size of the models and complexity of the GB region. For example, little is known about the stability of different GB types, their structures, and whether they have midgap states that can harm the optical absorption of solar cells. In this article, we address this research gap and systematically investigate the nature of GBs in cesium lead halides (CsPbX₃, X = Cl, Br, and I) and explore their potential energy surfaces. We choose the all-inorganic CsPbX₃, because these materials have similar properties with MAPbX₃, but structurally are much simpler which makes them more amenable to first-principles computational investigations. We first generate different GB structures using the coincidence site lattice (CSL) model. Then we search for the ground-state GB structure by crystal shift and lattice expansion as we discuss later. Here we thoroughly investigate the optimum structure of the GB region and determine its local crystal structure, which is relevant for interpreting experimental measurements. The changes in the local electrostatic potential across a GB can be due to bound excess charges in the GB region, or to changes in the local structure and atomic density in the GB region. For instance, in CuGaSe2, an electrostatic potential well of the order of 0.2 V in depth is reported for Σ 3 GB and 0.8 V for Σ 9 GB. Schmidt et al. used DFT-based GB models and TEM images to argue that this difference is due to a reduced atomic density in the GB core, namely Cu atoms, because of the reconstruction of the polar surface.³³ Further, using the obtained optimum structure, we study the electronic and optical properties of the stable configurations and explore the GB effect on the bulk phase.

COMPUTATIONAL METHODS

Our density functional theory (DFT) calculations are carried out using the Vienna Ab-initio Simulation Package (VASP)^{34,35} employing the projector augmented wave (PAW) pseudopotentials^{35,36} and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional.³⁷ The plane-wave cutoff energy is 400 eV for geometric optimization and electronic properties calculations. All the systems are fully relaxed until the final force on each atom is less than 0.02 eV/Å. We use a supercell approach with periodic boundary conditions with two GBs per unitcell. Finite size effects are mitigated using a supercell with large lattice constant along the direction perpendicular to the GB. The Brillouin zone is sampled with 9 × 9 × 9 Monkhorst– Pack special *k*-point meshes³⁸ for bulk, and a 2 × 2 × 1 k-grid for supercells with GB where the gamma point sampling is in the direction perpendicular to the GB plane.

RESULTS AND DISCUSSION

The cubic structure (α phase) of CsPbX₃ has five atoms per unitcell with Pb and halogen ions respectively located at the body and face-center forming the corner-sharing PbX₆ octahedron, and Cs atoms at the corner of the cell. All the structures possess the Pm3m symmetry without any distortion, which are more ordered than that of MAPbX₃ (MA= CH₃NH₃) because unlike the randomly orientated MA molecule, the single Cs atom has no orientations. The optimized lattice constants listed in Table 1 are in good agreement with previous theoretical data,³⁹ and 2–4% overestimate the experimental values.⁴⁰ The computed cohesive

Table 1. Lattice Constants,	Cohesive Energy, and Tolerance
Factor of $CsPbX_3$ (X = Cl,	Br, and I) Cubic Perovskites

	CsPbCl ₃	CsPbBr ₃	CsPbI ₃
a (Å)	5.71 ^{<i>a</i>}	5.99 ^a	6.40 ^a
	5.61 ^b	5.87 ^b	6.18 ^b
	5.73 [°]	5.99 ^c	6.39 ^c
$E_{\rm c}~({\rm eV})$	-15.69	-14.34	-12.65
τ	0.93 ^d	0.92^{d}	0.89 ^d
^a This work. ^b Ref	32. ^c Ref 31. ^d Ref	42.	

energies of the three bulk phases (Table 1) show that these become less stable as the size of halogen atoms increases. This can be understood from Goldschmidt tolerance factor $\tau = \frac{R_A + R_g}{\sqrt{2}(R_B + R_\chi)}$ (*R* is atomic radii) that is expected to be close to 1 for the material to stabilize in the perovskite structure.^{41,42} As shown in Table 1, the value of τ decreases from Cl to I, displaying the same trend with the cohesive energy. CsPbI₃ has the smallest τ value indicating that Cs is still not large enough to hold the cubic PbI₆ framework although it is the largest alkali element. This explains why the cubic organic MAPbI₃ is a stable perovskite while as CsPbI₃ is not.⁵ As we dicsuss below, the structural stability of the pervoskites is crucial for understanding the GB energy.

In this study, we investigate the symmetric tilt boundaries of CsPbX₃ constructed by the CSL model, i.e., the two grains are tilted by a given angle until their surface planes coincide.⁴³ In particular, we focus on $\Sigma 3(111)$, $\Sigma 3(112)$, $\Sigma 5(210)$, and $\Sigma 5(310)$ GBs as these commonly appear in the oxide perovskite SrTiO₃,⁴⁴ have low GB energy,⁴⁵ and high strength.⁴⁶ Only stoichiometric boundaries are constructed, that is, the atomic ratio of Cs, Pb, and halogen remains unchanged as in the bulk phase. The structure of the isolated GB region is obtained by using a supercell approach where the lattice constant along the direction perpendicular to the GB plane is large enough. We find that the GBs have to be separated by more than 20 Å to mitigate the interactions between the two GBs in the supercell due to the use of periodic boundary conditions (see Figure S1).

The GB structures obtained using the CSL model are generally under strain due to unsaturated, wrong, or extra bonding in the GB region, which would lead to high GB energies. To obtain their optimum structures, within stoichiometric conditions, we map out the so-called γ surface⁴⁴ which measures the GB stability given that one grain can freely translate with respect to the other one by a two-dimensional vector l_{\parallel} parallel to the GB plane, and further that the lattice vector perpendicular to the GB plane can relax to release any residual strain. We gauge the stability by calculating the GB energy with respect to bulk phase, defined as

$$\sigma_{\rm GB} = \frac{E_{\rm GB} - E_{\rm bulk}}{2A}$$

where the $E_{\rm GB}$ and $E_{\rm bulk}$ are the total energy of the GB and its corresponding bulk supercell, and A is the area of GB plane. The factor of 2 accounts for the existence of two equivalent GBs in the supercell. The γ surface is mapped for different values of l_{\parallel} defined in the primitive unitcell of the bulk material. This exhaustive search is crucial for finding out the global energy minima as can be judged by inspecting the complexity of the obtained γ surface shown in Figure 1 (dark regions represent low $\sigma_{\rm GB}$ configurations).



Figure 1. γ Surface of (a) $\Sigma 3(111)$, (b) $\Sigma 3(112)$, (c) $\Sigma 5(210)$, and (d) $\Sigma 5(310)$ GBs. The darker color represents the structures with lower GB energy. The *x*- and *y*-axes measure the percentage shifts along the GB plane lattice coordinates, as indicated for each GB.

To better understand the procedure used in our GBstructure search, we take CsPbBr₃ $\Sigma 5(210)$ as an example. Figure 2 shows the structural relationship between two configurations $\Sigma 5(210)(0.4,0)$ and $\Sigma 5(210)(0,0)$ obtained with $l_{\parallel} = (0.4, 0)$ and the unshifted structure $l_{\parallel} = (0, 0)$.



Figure 2. Formation of unrelaxed $\Sigma 5(210)(0.4,0)$ boundary (bottom) from $\Sigma 5(210)(0,0)$ boundary (top) by shifting the rightside grain (indicated by purple rectangle) along the red-arrow direction by 40% of the [100] lattice constant while leaving the leftside grain fixed. Gray, blue, and red balls represent the Cs, Pb, and Br atoms, respectively. Here, rightside and leftside are not meaningful for periodic systems, but used for illustrative purposes only.

The notation $\Sigma 5(210)(0.4,0)$ indicates that we translate the grain located at right side of the supercell (see Figure 2) upward along [100] direction by 40% of the [100] vector length while leaving the left grain fixed throughout the simulation. After the shift, we find that the newly formed $\Sigma 5(210)(0.4,0)$ GB also has the mirror symmetry, but this symmetry plane is right shifted as compared to the initial one. The γ surface is obtained by relaxing the structure fixing [100] and [02-1] lattice vectors, while making several small increments along [012] direction to release the strain in direction perpendicular to the GB plane. The obtained lowest-energy structure is the optimum configuration with minimal strain perpendicular to the GB plane, and repulsion in GB region has been minimized to the largest degree.

Figure 1a shows that for $\Sigma 3(111)$, there exists two low σ_{GB} regions with nearly equal energies at $l_{\parallel} = (0, 0)$ and $l_{\parallel} = (0.5, 0.5)$ 0.5). Upon further inspection, we verified that the two configurations are indeed equivalent to each other sharing the same symmetry. Thus, there is only one unique stable configuration $\Sigma 3(111)(0,0)$ for the $\Sigma 3(111)$ GB. For $\Sigma_3(112)$, we also observed two low-energy configurations, respectively located at $l_{\parallel} = (0, 0)$ and $l_{\parallel} = (0.66, 0)$. However, these two configurations are distinct from each other as shown in Figure 1b, since $\Sigma 3(111)(0,0)$ and $\Sigma 3(111)(0.66,0)$ possess different mirror and mirror-glide symmetries. Similarly, this is the case in $\Sigma 5(210)$ GB. By shifting one grain by $l_{\parallel} = (0.4, 0)$, i.e., along [100] by 40%, we obtain the global minima, while the unshifted $l_{\parallel} = (0, 0)$ is a metastable configuration. From the γ surface, we can see that $\Sigma 5(210)(0.4,0)$ boundary even has a lower energy than $\Sigma 5(210)(0,0)$ judging from the color (lower by 0.081 eV/Å²), implying that the grain shift can effectively weaken the repulsion in GB area, hence reduce σ_{GB} . For $\Sigma 5(310)$, the γ surface looks complicated, as there are many configurations with different l_{\parallel} but similar σ_{GB} . The lowest energy configuration is located at $l_{\parallel} = (0.5, 0)$. Interestingly, all the stable GB configurations prefer to have some structural symmetries (like mirror or mirror glide symmetry). These arguments based on symmetry were very instrumental in finding the global minimum energy for a given GB model, and reducing computational cost associated with searching for the optimum structure.

Using the approach discussed above, we obtain all the energetically stable configurations of the different GBs. Due to the structural similarity of bulk phases among the different $CsPbX_3$ (X = Cl, Br, and I), it is not surprising that the GB configurations are also similar. Figure 3 shows the optimized



Figure 3. Optimized stable CsPbX₃ (X = Cl, Br, and I) GB structures of $\Sigma_3(111)$, $\Sigma_3(112)$, $\Sigma_5(210)$, and $\Sigma_5(310)$. All the structures are relaxed by shift and lattice expansion as explained in main text. Gray, blue, and red balls represent the Cs, Pb, and X atoms, respectively. The purple circle (green rectangle) shows the unsaturated halogen (Pb) atoms.

structures of the four GB models in our study. With the exception of $\Sigma 3(111)$ boundary, all the other three GB structures have two distinct minima. Table 2 lists σ_{GB} of GB

Table 2. GB Energies of the Most Stable $CsPbX_3$ (X = Cl, Br, and I) GB Structures

		GB energy (J/m ²)		
GB type	tilt angle	CsPbCl ₃	CsPbBr ₃	CsPbI ₃
$\Sigma 3(111)(0,0)$	60.0°	0.056	0.039	0.034
$\Sigma 3(112)(0,0)$	60.0°	0.037	0.034	0.010
$\Sigma 3(112)(0.66,0)$		0.069	0.076	0.000
$\Sigma5(210)(0,0)$	36.9°	0.157	0.090	0.135
$\Sigma 5(210)(0.4,0)$		0.030	0.009	-0.032
Σ5(310)(0,0)	36.9°	0.123	0.089	-0.176
$\Sigma 5(310)(0.5,0)$		0.057	0.040	-0.024

structures in Figure 3. For CsPbCl₃ and CsPbBr₃, the GB energies show similar trends. For example, the most stable GB configuration is $\Sigma 5(210)(0.4,0)$. This can be understood by inspecting the structure of the GB (Figure 3) and noticing that atoms in the $\Sigma 5(210)(0.4,0)$ boundary region remain nearly the same as those in the bulk phase, which means that all GB atoms are saturated without any dangling bonds. Further, bond lengths between atoms in the GB region are also similar to those in the bulk phase. In contrast, for other GB structures, such as $\Sigma 5(210)(0,0)$, $\Sigma 5(310)(0,0)$, and $\Sigma 3(112)(0.66,0)$ boundaries, there are unsaturated halogen or Pb atoms (as indicated in Figure 3) with dangling bonds, which explain their high interface energy. The case of CsPbI₃ is somewhat special due to negative σ_{GB} for $\Sigma 5(210)(0.4,0)$, $\Sigma 5(310)(0,0)$, and Σ 5(310)(0.5,0). At first these negative values seem in error and nonphysical, but can be understood because the GB energy is measured with respect to the cubic bulk phase of CsPbI₃ that is unstable as discussed before. Although the structural instability of CsPbI3 leads to the abnormal GB energies, it is still useful to compare the results of CsPbI₃ with the other systems, because the properties of CsPbI₃ are similar to those of MAPbI₃, which will be discussed below.

In Figure 3, we notice that the "grain region" of most GB models has tetragonal- or orthorhombic-like reconstructions, namely the lead-halide-lead octahedral angle is different from 180° as those in cubic phase. This is because the cubic phase is not the most stable configuration at zero temperature in DFT calculations. The GBs are constructed from the primitive cubic cell, but these are expected to reconstruct into the tetragonal or orthorhombic phase if the unitcell is enlarged. However, for some GBs we found only a partial reconstruction because the model is not large enough along all lattice directions.

The presence of GBs in silicon and other photovoltaic materials is generally detrimental to their photovoltaic properties because these create recombination centers due to midgap states. $^{17-21}$ To investigate the impacts of GBs on electronic properties of CsPbX₃ perovskites, we calculated the density of states (DOS) as well as the band-decomposed charge density of highest valence band (HVB) and lowest conduction band (LCB). Figure 4a shows the electronic structures of different GBs in CsPbBr₃, all of which show the absence of midgap states. This is clearly very favorable for solar cell applications, which make these perovskites much better than conventional semiconductors like Si²² and CdTe,⁴⁷ where GB defects decreases their solar conversion efficiency. CsPbCl₃ and CsPbI₃ display similar behavior as shown in Figure S2 and S3. Thus, we conclude that the GB effect on their electronic properties is benign. To further confirm this conclusion, we also calculated the imaginary part of dielectric function of different GBs of CsPbBr₃ as well as the bulk phase, as shown in Figure 4b. The absorption curve of bulk CsPbBr₃ agrees with previous study, which shows relatively large absorption in visible region.³⁹ For GB structures, we see that the normalized absorption curve of all the models are quite similar to the case of the bulk, further confirming the weak effect of GBs on electronic structure. Although there is no obvious change in the absorption spectra, there is a slight down-shift of the intensity at the absorption peak in $\Sigma 5(210)(0,0)$ and $\Sigma 5(310)(0,0)$. These GB models have the highest GB energy, which as Figure 3 shows, these have unsaturated halogen atoms in the GB regions. Further, these dangling bonds lead to a shallow trap states, which decrease the intensity. For the low-energy GBs, the position and intensity are similar to the corresponding bulk

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Figure 4. (a) Electronic density of states of different GB structures in CsPbBr₃. Band decomposed charge density of highest valence band (HVB) and lowest conduction band (LCB) are plotted in the inset image. (b) Imaginary part of dielectric function of bulk CsPbBr₃ as well as the GB structures.

values. Thus, we conclude that GBs in CsPbX₃ perovskites have no harmful effects on electronic and optical properties, which is beneficiary to optoelectronic applications.

Although we do not observe midgap states in all models, there exist shallow states (Figure 4) near the VBM in some GBs, which will increase the effective mass of holes as argued recently in Yin's work.³² In Figure S4, we plot the difference of DOS between the GB structure and the bulk phase of CsPbBr₃, where the positive and negative values represent the increase and the decrease of DOS at a certain energy level. We find that $\Sigma 5(210)(0,0)$ and $\Sigma 5(310)(0,0)$ have the largest DOS increase near VBM, resulting from the dangling bonds in the GB regions. For others, due to the crystal shift and lattice expansion, the DOS difference between GB structure and the bulk phase is very small. We even observe DOS decrease in some GBs, like $\Sigma 3(111)$ and $\Sigma 5(310)(0.5,0)$, which leads to a small carrier effective mass, hence increasing the mobility.

Previous reports demonstrated that dangling bonds, wrong bonds, and extra bonds are the general features of GBs, which is the origin of midgap states.^{24,47} Therefore, it can be argued that the absence of deep levels in $\Sigma 3(111)(0,0)$, $\Sigma 3(112)(0,0)$, and $\Sigma 5(210)(0.4,0)$ is due to lack of dangling bonds. Figure 3 shows that the atoms in GB region of these structures are all fully coordinated like those in bulk phase, and the charge densities of HVB and LCB in boundary region are, with little differences, similar to those in the bulk structure. Indeed these three GBs are relatively stable with lowest GB energy as shown in Table 2 because of the similarities in their (electronic) structure to the bulk phase. However, for the other GBs, $\Sigma_3(112)(0.66,0), \ \Sigma_5(210)(0,0)\Sigma_5(210)(0,0), \ \Sigma_5(310)(0,0),$ and $\Sigma 5(310)(0.5,0)$, dangling and wrong bonds are observed in their optimized structures (see Figure 3), and thus midgap states are likely to exist. However, this turns out not to be the case. To understand this, it is useful to draw an analogy with CdTe. Previous study on CdTe GBs showed that the strong Te-Te interactions create antibonding $pp\sigma^*$ as deep levels in their band structure, because the distance of Te-Te dangling bond (3.47 Å) is much shorter than that of Te-Te bond (4.55 Å) in the bulk phase.⁴⁸ In contrast in CsPbX₃ the anion–anion interaction is relatively weak as we observed in all of the models, owing to the large distance between unsaturated

halogen atoms. This feature leads to the absence of midgap states in these systems. For instance, the Cl–Cl pair at the GB area is separated by 3.51 Å, which is beyond the interaction range of Cl⁻ ions. For CsPbBr₃ and CsPbI₃ systems, which also adapt similar configurations to CsPbCl₃, but have a larger lattice constant (Table 1) than that of CsPbCl₃, the interactions between Br–Br and I–I pair are even weaker, which explains why midgap states are also absent.

To corroborate our findings and shed light on the origin of midgap states, we further calculated the partial DOS (PDOS) of GB without crystal shift and lattice expansion. Here, we take CsPbCl₃ Σ 5(210)(0,0) as the example, because the lattice constant of CsPbCl₃ is smallest among CsPbX₃, and this GB structure contains both Cl and Pb dangling bonds, which is representative of other models. Figure 5 shows the comparison between electronic structures of the bulk, unrelaxed, and fully optimized CsPbCl₃ $\Sigma 5(210)(0,0)$ GB. First, we compare the PDOS of the bulk and unrelaxed structures (Figure 5a,b). For the valence band, we observe a peak near the Fermi level of the unrelaxed GB model, which is absent in the bulk phase. This peak is contributed by the *p* orbitals of Cl atoms in GB region, implying that although the interaction of Cl dangling bonds exists, it is not strong enough to move into the band gap. Another peak is found near the edge of the conduction band, which originates from the p orbitals of Pb atoms in the GB region. However, this midgap state disappears after lattice expansion at which this peak moves into the conduction band. The underpinning of this behavior is that before lattice expansion, the Pb-Pb distance in the GB region is 3.40 Å, which is much shorter that in the relaxed structure (4.15 Å). This strong repulsion between the two Pb atoms shifts the level deep in the band gap. Similar phenomenon was also observed in CuInSe₂ GB system, because Se-Se wrong bonding is also energetically very unfavorable.²⁴ We also find that the midgap state created by the Cl dangling bonds in unrelaxed structure also disappears in the fully relaxed structure for similar reasons. Therefore, we conclude that the reason for the absence of deep levels generated by GB in halide perovskites is the large distance between unsaturated atoms in these systems and the atomic reconstruction during the formation of stable GB configurations.



Figure 5. Calculated partial density of states of (a) bulk $CsPbCl_3$ perovskite, (b) unrelaxed, and (c) relaxed $\Sigma 5(210)(0,0)$ boundary structures. The Pb and Cl atoms are in the GB region.

Our findings establish the overall benign nature of the GBs in $CsPbX_3$ perovskites on their optical properties. It will be of interest to investigate the transferability of these findings to the organic perovskites, which share many similarities with $CsPbX_3$ except that the *A* cation (Cs) is replaced by an organic molecule (MA). We choose the most stable $CsPbI_3 \Sigma5(210)$ -(0.4,0) as an example, because for the bulk phase, the lattice constants of cubic $CsPbI_3$ and MAPbI₃ are very close. Figure 6a

and 6b show the geometric structures of $\Sigma 5(210)(0.4,0)$ boundary of cubic CsPbI₃ and MAPbI₃, where they share similar configurations in the GB region. Also, both structures show similar characters in their electronic properties as exemplified by having nearly the same total DOS, without any deep levels (see Figure 6c,d). Further, for both cases, the edge of valence band is contributed by the *p* orbitals of I atoms in the GB region, while the edge of conduction band comes from the p orbits of Pb atoms. The results are in agreement with the work of Yan's group, which investigated the Σ 5(310)(0,0) GB^{5,7} and showed the absence of midgap states. Electronic structure determines the energy, optical and other properties of the material, therefore the similarity of electronic structures of GB in cubic CsPbI3 and MAPbI3 can guide us to study the GB properties of organic perovskite from the inorganic one, which is important in computational studies.

CONCLUSION

In summary, we carried out first-principles calculations of different GBs in all-inorganic CsPbX₃ (X = Cl, Br, and I) perovskites. The energetically favorable structures are located by exploring the γ surface of initial configurations constructed using the CSL model with small sigma values. The calculated GB energy shows that the most stable configuration is Σ 5(210)(0.4,0) for CsPbCl₃ and CsPbBr₃, and both systems exhibit similar trends. However, GB energies are abnormal in CsPbI₃ due to the negative values in some GB structures, which results from the structural instability of its cubic bulk phase. The electronic properties confirm that all the GBs in halide perovskites do not create midgap states in fundamental band gap, because of the large distance between unsaturated atoms and the atomic relaxation in forming the stable GB configurations. We further compare the geometric and electronic structures of GBs in CsPbI3 and MAPbI3. Results show that both structures share very similar properties, which can guide us to understand the GB properties of organic perovskites from the inorganic ones.



Figure 6. Geometric structures of $\Sigma 5(210)(0.4,0)$ boundary in (a) CsPbI₃ and (b) MaPbI₃. (c) and (d) are the corresponding electronic DOS of both structures. The partial DOS accounts for atoms in the GB region.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b11434.

Variation of grain boundary energy with respect to the distance between neighboring grain boundaries in a unitcell, GB energies of the most stable $CsPbX_3$ (X = Cl, Br, and I) GB structures, energy reference is tetragonal $CsPbX_3$ (X = Cl, Br, and I), total electronic density of states of different grain boundary structures in $CsPbCl_3$ and $CsPbI_3$, and the difference of DOS between the GB structure and the bulk phase of $CsPbBr_3$ (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Liu, M.; Johnston, M. B.; Snaith, H. J. Efficient Planar Heterojunction Perovskite Solar Cells by Vapour Deposition. *Nature* **2013**, *501*, 395–398.

(2) Green, M. A.; Ho-Baillie, A.; Snaith, H. J. The Emergence of Perovskite Solar Cells. *Nat. Photonics* **2014**, *8*, 506–514.

(3) Grätzel, M. The Light and Shade of Perovskite Solar Cells. *Nat. Mater.* **2014**, *13*, 838–842.

(4) Park, N.-G. Organometal Perovskite Light Absorbers toward a 20% Efficiency Low-Cost Solid-State Mesoscopic Solar Cell. J. Phys. Chem. Lett. 2013, 4, 2423–2429.

(5) Yin, W.-J.; Yang, J.-H.; Kang, J.; Yan, Y.; Wei, S.-H. Halide Perovskite Materials for Solar Cells: A Theoretical Review. *J. Mater. Chem. A* **2015**, *3*, 8926–8942.

(6) De Wolf, S.; Holovsky, J.; Moon, S.-J.; Löper, P.; Niesen, B.; Ledinsky, M.; Haug, F.-J.; Yum, J.-H.; Ballif, C. Organometallic Halide Perovskites: Sharp Optical Absorption Edge and Its Relation to Photovoltaic Performance. J. Phys. Chem. Lett. **2014**, *5*, 1035–1039.

(7) Yin, W. J.; Shi, T.; Yan, Y. Unique Properties of Halide Perovskites as Possible Origins of the Superior Solar Cell Performance. *Adv. Mater.* **2014**, *26*, 4653–4658.

(8) Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C. Long-Range Balanced Electron-and Hole-Transport Lengths in Organic-Inorganic CH₃NH₃PbI₃. *Science* **2013**, *342*, 344–347.

(9) Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J. Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber. *Science* **2013**, *342*, 341–344.

(10) Wang, Y.; Li, X.; Song, J.; Xiao, L.; Zeng, H.; Sun, H. All-Inorganic Colloidal Perovskite Quantum Dots: A New Class of Lasing Materials with Favorable Characteristics. *Adv. Mater.* **2015**, *27*, 7101–7108.

(11) Lignos, I.; Stavrakis, S.; Nedelcu, G.; Protesescu, L.; deMello, A. J.; Kovalenko, M. V. Synthesis of Cesium Lead Halide Perovskite Nanocrystals in a Droplet-Based Microfluidic Platform: Fast Parametric Space Mapping. *Nano Lett.* **2016**, *16*, 1869–1877.

(12) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites ($CsPbX_3$, X=Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, *15*, 3692–3696.

(13) Song, J.; Li, J.; Li, X.; Xu, L.; Dong, Y.; Zeng, H. Quantum Dot Light-Emitting Diodes Based on Inorganic Perovskite Cesium Lead Halides (CsPbX₃). *Adv. Mater.* **2015**, *27*, 7162–7167.

(14) Zhang, D.; Eaton, S. W.; Yu, Y.; Dou, L.; Yang, P. Solution-Phase Synthesis of Cesium Lead Halide Perovskite Nanowires. *J. Am. Chem. Soc.* **2015**, *137*, 9230–9233.

(15) Kulbak, M.; Cahen, D.; Hodes, G. How Important Is the Organic Part of Lead Halide Perovskite Photovoltaic Cells? Efficient CsPbBr₃ Cells. *J. Phys. Chem. Lett.* **2015**, *6*, 2452–2456.

(16) Dang, Y.; Liu, Y.; Sun, Y.; Yuan, D.; Liu, X.; Lu, W.; Liu, G.; Xia, H.; Tao, X. Bulk Crystal Growth of Hybrid Perovskite Material CH₃NH₃PbI₃. *CrystEngComm* **2015**, *17*, 665–670.

(17) Yin, W. J.; Wu, Y.; Wei, S. H.; Noufi, R.; Al-Jassim, M. M.; Yan, Y. Engineering Grain Boundaries in $Cu_2ZnSnSe_4$ for Better Cell Performance: A First-Principle Study. *Adv. Energy Mater.* **2014**, *4*, 1300712.

(18) Yin, W.-J.; Wu, Y.; Noufi, R.; Al-Jassim, M.; Yan, Y. Defect Segregation at Grain Boundary and Its Impact on Photovoltaic Performance of CuInSe₂. *Appl. Phys. Lett.* **2013**, *102*, 193905.

(19) Li, C.; Wu, Y.; Poplawsky, J.; Pennycook, T. J.; Paudel, N.; Yin, W.; Haigh, S. J.; Oxley, M. P.; Lupini, A. R.; Al-Jassim, M.; Pennycook, S. J.; Yan, Y. Grain-Boundary-Enhanced Carrier Collection in Cdte Solar Cells. *Phys. Rev. Lett.* **2014**, *112*, 156103.

(20) Zhang, L.; Da Silva, J. L.; Li, J.; Yan, Y.; Gessert, T.; Wei, S.-H. Effect of Copassivation of Cl and Cu on Cdte Grain Boundaries. *Phys. Rev. Lett.* **2008**, *101*, 155501.

(21) Yin, W.-J.; Shi, T.; Yan, Y. Superior Photovoltaic Properties of Lead Halide Perovskites: Insights from First-Principles Theory. J. Phys. Chem. C 2015, 119, 5253–5264.

(22) Raghunathan, R.; Johlin, E.; Grossman, J. C. Grain Boundary Engineering for Improved Thin Silicon Photovoltaics. *Nano Lett.* **2014**, *14*, 4943–4950.

(23) Seto, J. Y. The Electrical Properties of Polycrystalline Silicon Films. J. Appl. Phys. **1975**, 46, 5247–5254.

(24) Yan, Y.; Jiang, C.-S.; Noufi, R.; Wei, S.-H.; Moutinho, H.; Al-Jassim, M. Electrically Benign Behavior of Grain Boundaries in Polycrystalline CuInSe₂ Films. *Phys. Rev. Lett.* **2007**, *99*, 235504.

(25) Huang, J.; Shao, Y.; Dong, Q. Organometal Trihalide Perovskite Single Crystals: A Next Wave of Materials for 25% Efficiency Photovoltaics and Applications Beyond? *J. Phys. Chem. Lett.* **2015**, *6*, 3218–3227.

(26) de Quilettes, D. W.; Vorpahl, S. M.; Stranks, S. D.; Nagaoka, H.; Eperon, G. E.; Ziffer, M. E.; Snaith, H. J.; Ginger, D. S. Impact of Microstructure on Local Carrier Lifetime in Perovskite Solar Cells. *Science* **2015**, *348*, 683.

(27) Bi, C.; Wang, Q.; Shao, Y.; Yuan, Y.; Xiao, Z.; Huang, J. Non-Wetting Surface-Driven High-Aspect-Ratio Crystalline Grain Growth for Efficient Hybrid Perovskite Solar Cells. *Nat. Commun.* **2015**, *6*, 7747.

(28) Zhou, Y.; Game, O. S.; Pang, S.; Padture, N. P. Microstructures of Organometal Trihalide Perovskites for Solar Cells: Their Evolution from Solutions and Characterization. *J. Phys. Chem. Lett.* **2015**, *6*, 4827–4839.

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(29) Im, J.-H.; Jang, I.-H.; Pellet, N.; Grätzel, M.; Park, N.-G. Growth of CH₃NH₃PbI₃ Cuboids with Controlled Size for High-Efficiency Perovskite Solar Cells. *Nat. Nanotechnol.* **2014**, *9*, 927–932.

(30) Nie, W.; Tsai, H.; Asadpour, R.; Blancon, J.-C.; Neukirch, A. J.; Gupta, G.; Crochet, J. J.; Chhowalla, M.; Tretiak, S.; Alam, M. A.; Wang, H.-L.; Mohite, A. D. High-Efficiency Solution-Processed Perovskite Solar Cells with Millimeter-Scale Grains. *Science* **2015**, 347, 522–525.

(31) Yun, J. S.; Ho-Baillie, A.; Huang, S.; Woo, S. H.; Heo, Y.; Seidel, J.; Huang, F.; Cheng, Y.-B.; Green, M. A. Benefit of Grain Boundaries in Organic–Inorganic Halide Planar Perovskite Solar Cells. *J. Phys. Chem. Lett.* **2015**, *6*, 875–880.

(32) Yin, W. J.; Chen, H.; Shi, T.; Wei, S. H.; Yan, Y. Origin of High Electronic Quality in Structurally Disordered $CH_3NH_3PbI_3$ and the Passivation Effect of Cl and O at Grain Boundaries. *Adv. Electronic Mater.* **2015**, *1*, 1500044.

(33) Schmidt, S. S.; Abou-Ras, D.; Sadewasser, S.; Yin, W.; Feng, C.; Yan, Y. Electrostatic Potentials at Cu(In, Ga)Se₂ Grain Boundaries: Experiment and Simulations. *Phys. Rev. Lett.* **2012**, *109*, 095506.

(34) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 11169.

(35) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 1758.

(36) Blöchl, P. E. Projector Augmented-Wave Method. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 50, 17953.

(37) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(38) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188.

(39) Lang, L.; Yang, J.-H.; Liu, H.-R.; Xiang, H.; Gong, X. First-Principles Study on the Electronic and Optical Properties of Cubic ABX₃ Halide Perovskites. *Phys. Lett. A* **2014**, *378*, 290–293.

(40) Akkerman, Q. A.; D'Innocenzo, V.; Accornero, S.; Scarpellini, A.; Petrozza, A.; Prato, M.; Manna, L. Tuning the Optical Properties of Cesium Lead Halide Perovskite Nanocrystals by Anion Exchange Reactions. J. Am. Chem. Soc. **2015**, 137, 10276–10281.

(41) Chen, Q.; De Marco, N.; Yang, Y. M.; Song, T.-B.; Chen, C.-C.; Zhao, H.; Hong, Z.; Zhou, H.; Yang, Y. Under the Spotlight: The Organic–Inorganic Hybrid Halide Perovskite for Optoelectronic Applications. *Nano Today* **2015**, *10*, 355–396.

(42) Travis, W.; Glover, E.; Bronstein, H.; Scanlon, D.; Palgrave, R. On the Application of the Tolerance Factor to Inorganic and Hybrid Halide Perovskites: A Revised System. *Chemical Science* **2016**, *7*, 4548.

(43) Ogawa, H. Gbstudio: A Builder Software on Periodic Models of Csl Boundaries for Molecular Simulation. *Mater. Trans.* **2006**, 47, 2706–2710.

(44) Benedek, N. A.; Chua, A. L.-S.; Elsässer, C.; Sutton, A. P.; Finnis, M. W. Interatomic Potentials for Strontium Titanate: An Assessment of Their Transferability and Comparison with Density Functional Theory. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, 78, 064110.

(45) Kutsukake, K.; Usami, N.; Ohno, Y.; Tokumoto, Y.; Yonenaga, I. Control of Grain Boundary Propagation in Mono-Like Si: Utilization of Functional Grain Boundaries. *Appl. Phys. Express* **2013**, *6*, 025505.

(46) Straumal, B.; Polyakov, S.; Mittemeijer, E. Temperature Influence on the Faceting of Σ_3 and Σ_9 Grain Boundaries in Cu. *Acta Mater.* **2006**, *54*, 167–172.

(47) Yan, Y.; Al-Jassim, M.; Jones, K. Passivation of Double-Positioning Twin Boundaries in Cdte. J. Appl. Phys. 2004, 96, 320–326.

(48) Feng, C.; Yin, W.-J.; Nie, J.; Zu, X.; Huda, M. N.; Wei, S.-H.; Al-Jassim, M. M.; Yan, Y. Possible Effects of Oxygen in Te-Rich $\Sigma 3$ (112) Grain Boundaries in Cdte. *Solid State Commun.* **2012**, *152*, 1744–1747.