Halide-Dependent Electronic Structure of Organolead Perovskite Materials

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ABSTRACT: Organometal halide perovskites have recently attracted tremendous attention both at the experimental and theoretical levels. These materials, in particular methylammonium triiodide, are still limited by poor chemical and structural stability under ambient conditions. Today this represents one of the major challenges for polycrystalline perovskite-based photovoltaic technology. In addition to this, the performance of perovskite-based devices is degraded by deep localized states, or traps. To achieve better-performing devices, it is necessary to understand the nature of these states and the mechanisms that lead to their formation. Here we show that the major sources of deep traps in the different halide systems have different origin and character. Halide vacancies are shallow donors in I-based perovskites, whereas they evolve into a major source of traps in Cl-based perovskites. Lead interstitials, which can form lead dimers, are the dominant source of defects in Br-based perovskites, in line with recent experimental data. As a result, the optimal growth conditions are also different for the distinct halide perovskites: growth should be halide-rich for Br and Cl, and halide-poor for I-based perovskites. We discuss stability in relation to the reaction enthalpies of mixtures of bulk precursors with respect to final perovskite product. Methylammonium lead triiodide is characterized by the lowest reaction enthalpy, explaining its low stability. At the opposite end, the highest stability was found for the methylammonium lead trichloride, also consistent with our experimental findings which show no observable structural variations over an extended period of time.

Research in organometal halide solar cells has been burgeoning in the past few years following recent breakthroughs in power conversion efficiencies (PCE). Most research studies focused on methylammonium (MA) lead triiodide (MAPbI3) perovskite because of its optimal bandgap and its compatibility with solution-based processing. Br-based perovskites have also garnered interest, whereas pure Cl-based perovskites have been explored to a limited extent. Br- and Cl-based platforms, thanks to their wider bandgap, hold great promise in the fields of photocatalysis and photodetection.

It is known that Br/Cl-perovskites are more stable under ambient conditions, whereas it was shown that the introduction of Cl during MAPbI3 formation enhances the performance of photovoltaic devices. This raises important questions regarding the mechanisms that control the stability and defect physics in the different halide perovskites. In this work we explore the effect of halide replacement in organolead perovskite materials. Particularly, we focus on the defect physics of halide perovskite phases MAPbX3 including X = I, Cl, Br and the possible role of Cl in the MAPbI3 perovskite. In addition, we analyze the stability of perovskite compounds in terms of reaction enthalpies with respect to precursor phases. Our results reveal remarkable differences between different halide systems, and suggest distinct optimal growth conditions for each perovskite system.

We performed density functional theory (DFT) calculations whose details can be found in the Methods section. The notation used for defect classification is as follows: vacancies (VPb, VX), interstitials (Pbi, Xi), and antisites (PbX, PXb), where in the latter case AX indicates that A is substituted by B and X is the halogen species (I, Br, or Cl). We have concentrated mainly on the metal-halide related defects, because their growth condition (halide-poor/halide-rich) can readily be controlled by choosing different lead halide precursors. We have

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concentrated mostly on the deep defects that were related to these lead-halide ions.\textsuperscript{4,18,19}

To validate our model and correlate it to experimental results, we first calculated the density of states (DOS) of MAPbX\textsubscript{3}. Figure 1 shows the density of states of the tetragonal MAPbI\textsubscript{3} and cubic MAPbBr\textsubscript{3} and MAPbCl\textsubscript{3} room-temperature phases. The bandgap is in line with experimental values\textsuperscript{20} and follows the well-known trend going from I to Cl. The increase in bandgap is attributed to the decrease in lattice parameter along with a larger compressive strain\textsuperscript{20} which leads to higher wave function overlap and, as a result, higher orbital coupling. Moreover, the differences caused by similarly sized cations, i.e., formamidinium (FA) and MA cations, and different\textsuperscript{22} crystal structures (tetragonal and cubic), can be ascribed to tilting of the PbI\textsubscript{6} octahedra. This tilting has an impact on the Pb─I bond lengths and angles, as these affect the wave function overlap, which leads to the change in bandgap. Further, because the VBM is built upon hybridization between Pb 6s and X(3p\textsubscript{z},4p\textsubscript{z}) orbitals with mainly X(3p\textsubscript{z},4p\textsubscript{z}) character, it is reasonable to expect that going from I to Cl, the weight of the X molecular orbitals (MO) should increase. This impacts the ionization potential (the HOMO with respect to the vacuum) as demonstrated in recent work of Butler et al.\textsuperscript{23} Figure 2 shows the relative band alignment of MAPbBr\textsubscript{3} and MAPbCl\textsubscript{3} compounds with respect to MAPbI\textsubscript{3}. To align them, we have used the common, deep-lying Pb 5d levels as a reference.\textsuperscript{24} We find that the bandgap increment from I to Br to Cl is symmetrically driven by a concomitant downshift of the valence band and an upshift of the conduction band. This result is in good agreement with previously published results\textsuperscript{23--25} on the alignment of the valence and conduction bands.

Next, we turn our attention to the defect physics in all three organometal halide systems. Although previous studies\textsuperscript{4,11,18} have charted the defect levels of the MAPbI\textsubscript{3}, reports are scarce for MAPbBr\textsubscript{3} or MAPbCl\textsubscript{3}, motivating our theoretical study presented hereafter. The thermodynamic defect transition
levels are defined as points of equal formation energies\textsuperscript{26} for different charged states. These levels are strong indicators of whether the defects states will be deep or shallow: deep for stable charged states over the bandgap; shallow for close-to-the-bandedge states. DFT eigenvalues are shown in Figure 3 as solid for near-bandedge states and dashed lines for in-gap states.

We then turned to examine the defect formation energy diagrams for halide-rich and halide-poor growth conditions. The two scenarios are presented in Figure 3: halide-rich (Pb-poor) on the left and halide-poor (Pb-rich) on the right. Given that strictly halide-rich and Pb-rich conditions would correspond to the halide precursor in solid (I\textsubscript{2}), liquid (Br), or gaseous (Cl\textsubscript{2}) form, and Pb in fcc form, respectively, they

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Figure 3. Defect formation energies under halide rich conditions for: (a) tetragonal MAPbI\textsubscript{3}; (c) cubic MAPbBr\textsubscript{3}; and (e) cubic MAPbCl\textsubscript{3} perovskite phases. Defect formation energies under halide-poor environments for: (b) tetragonal MAPbI\textsubscript{3}; (d) cubic MAPbBr\textsubscript{3}; and (f) cubic MAPbCl\textsubscript{3} perovskite phases.
rather serve as two extreme cases. Nonetheless, our analysis reveals which conditions halide-poor or halide-rich are preferable for the purposes of attaining a low trap density.

From Figure 3, it is apparent that in the case of MAPbI₃ and MAPbBr₃, the dominant defect under halide-rich conditions is the lead vacancy (V_{Pb}'). In the case of MAPbCl₃, Pb₁⁺antisite is the dominant defect state. Surprisingly, the PbCl₁⁻antisite defect in cubic MAPbCl₃ is a shallow acceptor with a most stable charge state of −3. For this defect state, the situation is drastically different in the case of MAPbI₃, a fact which can be attributed to the fact that the tetragonal symmetry has a large relaxation energy (or large negative correlation energy U, negative effect) that stabilizes the neutral state of the PbI antisite. This can be further clarified by looking at the work of Yin et al., where no stabilization of the neutral state was found to occur in the cubic phase of the MAPbI₃. This is in line with our previous calculations, where two unique PbI antisites have been identified, one of which (in-plane) is in close agreement with previously published work. The lead antisites (Pb₀⁺, PbCl⁻, PbBr⁻) in the case of MAPbBr₃ and MAPbCl₃ are also defects with with −3 stable charge state and negative U behavior since the correlation energies are U = −1.63 eV and U = −0.7 eV, respectively. The correlation energies are defined as $U = \varepsilon(-1/2) - \varepsilon(-2/3)$, where $\varepsilon$ is the thermodynamic transition level of the corresponding charged states. In the diagrams of Figure 3, thermodynamic transition levels occur at those locations where the first derivative has a discontinuity. Lead antisites in the case of cubic MAPbBr₃ and tetragonal MAPbI₃ phases possess a deep-trap character associated with formation of linear trihalide ions, i.e., Br⁻ and I⁻. It is interesting to note that in the case of MAPbCl₃ and MAPbBr₃, trihalide ions are formed only with charged state −1, whereas in the case of MAPbI₃, triiodide ions can be formed with −3, −2, and −1 charged states. In the case of cubic MAPbBr₃, the PbBr₁⁻antisite is a deep acceptor with very high thermal ionization energy, in contrast with the case of MAPbCl₃, where the acceptor thermal ionization energy is very low.

In another major difference between tetragonal MAPbI₃ and cubic MAPbBr₃ and MAPbCl₃ phases, halide vacancies (V_{Br}, V_{Cl}) exhibit deep-trap behavior compared to V_{Pb}. This difference is attributed to the fact that transition level $\varepsilon(0/+1)$ of V_{Pb} in MAPbI₃ is located in the conduction band (CB), leading to hybridization between singly occupied neutral defect state and states near the CB edge. As a result, it is resonance within the conduction band minimum (CBM). Figure 3 shows that the thermal ionization level $\varepsilon(0/+1)$ found approximately 1.8 eV above the valence band maximum (VBM) for all halide vacancies (V_{Br}, V_{Cl}), thus leading to deep-trap behavior in MAPbBr₃ and MAPbCl₃ due to their wider bandgap. The wave function analysis of the V_{Br} and V_{Cl} states reveals localized $\sigma$ bond hybridization between nearest neighbor Pb(6p₀)-I(3p) and Pb(6p₀)-Cl(3p) orbitals as shown in Figure 4. The position of the defect state is affected by both the Pb(6p₀)-Br(6p₀) hybridization strength as well as by flattening of the [BrX₃]⁻ network going from Br to Cl (which is reflected in angle X-Br-X being equal to 164° and 166° for Br and Cl, respectively), which affects CBM location.

Note that the interstitial defects (I⁺, Br⁺, Cl⁻) are negative U defects but only the charge state +1 is stable and close to the VBM in the case of iodide and bromide perovskites. The localization (X (4p₁5p₂)-X (4p₁5p₂), $\sigma^*$) and relaxation pattern of the X⁺ states are very similar to those of the antisite defect, a finding that is in agreement with previously published results. On the other hand, the thermodynamic transition level ($\varepsilon(-1/+1)$) of Cl⁻ is located inside the valence band of MAPbCl₃, leaving only charged state −1 stable over the entire bandgap.

In addition to individual defect states, we have also calculated the binding energy of complex defects such as Pbₓ and Xₚb antisites for various charged states and according to

$$E_b[(V_{Pb} + X_i)^q] = H_i[V_{Pb}^q] - H_i[V_{Pb}^q(X)] - H_i[X_i^q]$$  \hspace{1cm} (1)

$$E_b[(V_{X} + Pb_i)^q] = H_i[V_{X}^q] - H_i[V_{X}^q(X)] - H_i[Pb_i^q]$$  \hspace{1cm} (2)

where $E_b$ is the defect binding energy, whereas $H_i$ is the defect formation energy of the various defects in the various q, m, n, charged states, where q = m + n, X = I, Br, Cl. We adopt the convention that negative (positive) binding energies indicate stable (unstable) complexes. In addition, the reaction pathways for defect complexes are not unique, i.e., there are many possibilities to satisfy the condition q = m + n as can be seen from Table 1, where, for example, PbBr₂ can have 3 possible decomposition pathways. It is important to note that the defect complex is stable only if all decomposition pathways are unfavorable. For example, in the case of the PbBr antisite, as can be seen from Table 1, the only complex that might appear stable is PbBr₂; however, it would decompose into the most stable V_{Pb} and Br⁺. Thus, no complexes are stable, i.e., PbBr decomposes into a lead vacancy (V_{Pb}) and a Br-interstitial (Brᵢ) and Br_{Br} decomposes into a bromide vacancy (V_{Br}) and Pb-interstitial (Pbᵢ).

One should keep in mind that the above considerations do not imply that defect complexes such as PbBr and Brₚb antisites will not be formed during perovskite crystallization. These metastable defect complexes will form and their concentration will depend on the defect formation energy; however, they will tend to decompose by overcoming kinetic barriers through energy supplied via thermal annealing or light soaking. Brᵢ in the oxidation state +1 has a very narrow stability region in the case of extreme p-type doping; thus it is unstable over nearly the entire bandgap (intrinsic to lightly doped conditions). In case of the Brₚb defect complex, Table 1 shows
Table 1. Defect Binding Energies for the Defect Complexes in MAPbI₃, MAPbBr₃, and MAPbCl₃ Perovskites

<table>
<thead>
<tr>
<th>defect complex</th>
<th>decomposition</th>
<th>binding energy, eV</th>
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<tbody>
<tr>
<td>Pb₂⁺</td>
<td>Ṽ₂⁺ Br⁻</td>
<td>2.358</td>
</tr>
<tr>
<td>Pb⁻</td>
<td>Ṽ₂⁺ Br⁻</td>
<td>1.836</td>
</tr>
<tr>
<td>Pb⁺</td>
<td>Ṽ₂⁺ Br⁻</td>
<td>0.620</td>
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<tr>
<td>Br₂⁺</td>
<td>Ṽ₂⁺ Pb²⁻</td>
<td>1.294</td>
</tr>
<tr>
<td>Br⁺</td>
<td>Ṽ₂⁺ Pb²⁻</td>
<td>1.329</td>
</tr>
<tr>
<td>Br⁻</td>
<td>Ṽ₂⁺ Pb²⁻</td>
<td>0.421</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>Ṽ₂⁺ Cl⁺</td>
<td>0.827</td>
</tr>
<tr>
<td>Pb⁻</td>
<td>Ṽ₂⁺ Cl⁺</td>
<td>0.078</td>
</tr>
<tr>
<td>Pb⁺</td>
<td>Ṽ₂⁺ I⁻</td>
<td>0.070</td>
</tr>
<tr>
<td>Br₂⁺</td>
<td>Ṽ₂⁺ Cl⁺</td>
<td>2.390</td>
</tr>
<tr>
<td>Br⁺</td>
<td>Ṽ₂⁺ Cl⁺</td>
<td>0.850</td>
</tr>
<tr>
<td>Br⁻</td>
<td>Ṽ₂⁺ Cl⁺</td>
<td>0.190</td>
</tr>
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</table>

that Br₁³⁺ and Br₂⁺ defects decompose most favorably into Ṽ₂⁺ and either Pb⁺⁺ or Pb⁺ thus leaving the only major deep defect, Pb₂ which could in turn could dimerize with another Pb atom. These results are in agreement with experimental studies which associate deep electron trapping to Pb₂ dimers and Pb cations. Similar analysis for the Pb₂⁺ and Cl₂⁻ species suggests that the only significantly contributing deep defect is the chloride vacancy (Ṽ₂⁺). This also sheds light on the question of the role of chloride in the mixed halide perovskites i.e. MAPbI₃–Cl. Having chloride in the mixed perovskite does not introduce additional deep trapping centers. In the case of MAPbI₃, one should note that Pb₂⁺ antisite does not decompose into primitive species such as Ṽ₂⁺ and I⁻, and this makes the Pb₂⁺ antisite a major source of deep traps. By looking at Figure 3 it is apparent that the preferred conditions for growth in MAPbBr₃ and MAPbCl₃ are halide-rich environments. This is opposite to the pure MAPbI₃ case, where I-poor conditions are preferred in order to have trap free crystal.

Figure 5. Time evolution of the main XRD peak of the perovskite phase for: (a) MAPbI₃, (b) MAPbBr₃, and (c) MAPbCl₃.
other hand, no additional features are found over time for MAPbBr$_3$ and MAPbCl$_3$ films, consistent with our theoretical finding of stable MAPbBr$_3$ and MAPbCl$_3$ perovskites.

Table 2 summarizes our main findings.

<table>
<thead>
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<th>Table 2. Summary of Main Findings</th>
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<tr>
<td>key findings</td>
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<tr>
<td>preferred growth mode (PGM)</td>
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<td>major source of deep defects</td>
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<td>concentration of deep defects at PGM</td>
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<td>good values for the $E_b$ at PGM</td>
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<td>reaction enthalpy stability</td>
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The results presented in this study provide a unified view of the defect physics in the most common organometal halide perovskites. They are summarized in Table 2. Good values for the $E_b$ in PGM are defined as values of the Fermi level at which defect formation energy is sufficiently high to ensure significantly low defect concentrations (<1 × 10$^{13}$ cm$^{-3}$). The investigations demonstrate the effect of halide replacement on electronic structure and perovskite stability. Analysis of defect aggregation in terms of defect binding energies reveals that the major source of deep traps is markedly different for the distinct perovskite materials.

**METHODS**

Calculations were performed within DFT formalism using the Perdew–Burke–Ernzerhof (PBE) GGA exchange correlation functional. Calculations were performed with the help of the CP2K package within Gaussian-augmented plane waves (GAPW) dual basis set using the molecularly optimized MOLOPT double $\zeta$-valence polarized (nDZVP) basis set implemented in CP2K code, which has a very small BSSE errors in gas and condensed phases. The plane-wavenumber cutoff was 300 Ry, which is suitable for the Goedecker–Teter–Hutter pseudopotentials. Periodic boundary conditions were used in all calculations. Spin-polarized (LSDA) and spin-unpolarized calculations (LDA) were performed in the case of the odd—-even number of electrons. The structural minimization was performed with the help of the Broyden-Fletcher-Goldfarb-Shanno algorithm (BFGS). Lattice constants were optimized and used throughout the calculations. The structural optimization was considered converged if the forces acting on the atoms were those with less than 0.04 eVÅ$^{-1}$. CP2K is a Γ-point code, therefore a sufficient number of unit cells is required to guarantee the convergence. For the MAPbI$_3$ material we have used 3 × 3 × 4 supercell (1728 atoms) of the original tetragonal unit cell, whereas for the MAPbBr$_3$ and MAPbCl$_3$ we have used 4 × 4 × 4 supercell composed of the original cubic cell. It was found that energy per primitive unit cell has converged to the error less than 10 meV/u.cell for the MAPbI$_3$ and MAPbCl$_3$ within the calculations. Therefore, the energy per primitive unit cell was 300 Ry, which is suitable for the Goedecker–Teter–Hutter pseudopotentials.

The authors declare no competing financial interest.

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**REFERENCES**


(23) Butler, K. T.; Frost, J. M.; Walsh, A. Band Alignment of the Hybrid Halide Perovskites CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}, CH\textsubscript{3}NH\textsubscript{3}PbBr\textsubscript{3} and CH\textsubscript{3}NH\textsubscript{3}PbCl\textsubscript{3}. Mater. Horiz. 2015, 2, 228–231.

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