Adding to the Perovskite Universe: Inverse-Hybrid Perovskites

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Supporting Information

ABSTRACT: Perovskites are a rich family of functional materials with many interesting physical properties. Usually, they contain two cationic species on the A- and B-sites, surrounded by anionic species on the X-site, but compounds are also known that invert the ion types on the respective lattice sites (inverse perovskites). Recently, conventional perovskites with one inorganic cation substituted by an organic molecule were intensively studied due to the promising performance of CH$_3$NH$_3$PbI$_3$ based solar cells. Here, for the first time, we take the concept of inverse perovskites to organic–inorganic hybrid materials, investigating the properties of inverse-hybrid perovskites by first-principles calculations, adding yet another structural variant to the perovskite universe. We present results for various compositions with a wide range of band gaps from metallic systems over small and intermediate band gaps to large band gap semiconductors. Due to the changed location of the organic ion, the inverse structure could overcome stability problems of current hybrid perovskite photovoltaics. In addition, inverse-hybrid perovskites show inherent off-center displacement of ions, leading to polar phases with large polarization.

Perovskite materials exhibit fascinating properties for various applications, and a wide variety of different compositions have been investigated. The perovskite ABX$_3$ structure contains cations on the A- and B-sites, with anions on the X-site balancing the positive charges, leading to a crystalline solid with strong ionic bonding. Besides the numerous inorganic perovskites, over the past decade there has been resurgent interest in perovskites with organic molecules, forming so-called organic–inorganic hybrid perovskites (HPs). The organic part is usually employed on the A-site, forming materials with promising photophysical properties for photovoltaic applications, but can also be found on the X-site or a combination of both. However, it is also possible to invert the ionic charges, forming structures with anions on the A- and B-sites and cations on the X-site. Although less frequently investigated than perovskites, such inverse or antiperovskites (IPs) have been studied since 1980, showing many fascinating physical properties.

Herein, we combine the two concepts of hybrid and inverse perovskites, proposing a new class of inverse-hybrid perovskites (IHPs). We present results for a variety of different X,B, compounds combining X = CH$_3$NH$_3$ (MA) with monovalent (a$^-$) and divalent anions (a$^{2-}$) by accurate density functional calculations using QUANTUM ESPRESSO (for details on the computational setup see the Supporting Information (SI)). We demonstrate the flexibility of these compounds as well as their limitations to form the perovskite structure, estimate their formation energies, and show that the compositional variety leads to materials with metallic and semiconducting properties, with band gaps tunable from very small values due to spin–orbit coupling (SOC), over an intermediate range interesting for photovoltaic applications, up to wide band gap semiconductors. The structural alignment naturally includes a B-site off-center displacement, giving rise to polar structures.

Traditionally, the Goldschmidt tolerance factor is used as a key indicator for the preference of ABX$_3$ compositions to crystallize as a perovskite. This concept has also been extended to organic molecules in HPs. We can further extend this concept for IPs and IHPs. However, we must keep in mind that anionic radii are less established than cationic radii and that the tolerance factor is only an indicator, with acceptable values ranging typically from $t = 0.75 - 1.0$. Common X-site anions in perovskites have ionic radii of 1.26−2.06 Å (ionic radii between O$^{2-}$ and I$^-$). In order to be suitable to build perovskites with inorganic anions, we choose a small cation within this range for the X-site. Due to its favorable character for HPs and the current intense focus, we select MA. When calculating tolerance factors for structures that contain organic ions, complications arise because their effective ionic radii are less established and they are nonspherical. Because the organic cation in IHPs is...
located on the X-site and, thus, enters the calculation of \( t \) in the numerator and denominator, fortunately \( t \) is quite insensitive to the exact value of the effective ionic radius of the organic cation (see Table S11) and we can, therefore, use the proposed value of \( r_{\text{eff}}(\text{MA}) = 2.17 \text{ Å} \) with confidence.\(^{15}\)

Radii for untabulated anionic oxidation states were obtained similarly to Shannon’s original approach; see Table S12. We find that the resulting values for \( t \) are a good tool to estimate suitable ion compositions, which we will use below.

To pair with a monovalent cation for the X-site, we are seeking \( B^{-1/2} \) and \( A^{2−/1−} \) ions. On the one hand, \( A^{2−} \) ions should generally be larger than \( a^{−} \) anions and should favor the A-site. On the other hand, the B-site provides a closer proximity to the cations, which should be favorable for the anion in the higher oxidation state due to the greater Coulombic attraction. Thus, in contrast to conventional perovskites where these effects go hand in hand, they are competing in the case of IPs, and the preference of A- vs B-site occupation must be investigated.

Here, we focus on the most stable compositions of the materials with the most interesting properties, whereas details on our materials search will be discussed elsewhere.

Choosing \( A = \Gamma^− \) as a large anion provides structural flexibility, encouraging a search for suitable \( B^{2−} \) anions. Natural candidates are elements of the chalcogen group. For \( (\text{MA})_2\text{Bi} \), with \( B = \text{O, S, Se, Te} \), all compounds have tolerance factors within the range of 0.71–1.0 and could, therefore, form stable IHPs, with Te and Se compounds on the fringe where other candidate are elements of the chalcogen group. For \( (\text{MA})_2\text{Bi} \), we find a structure (Figure 1a,b) with both corner- and edge-sharing octahedra (CaIrO3 structure), which is energetically preferred by 0.32 eV per formula unit (f.u.) compared to the cubic perovskite structure. In fact, we find that this CaIrO3 phase is favored for all cases where the tolerance factor falls below a threshold of 0.76.

In the CaIrO3 structure, the large B−X bonding distance is better accommodated due to the stretching of bonds along one axis and a rotation of the BX2 plane by about 45° perpendicular to this axis. As a result, the H−N−H angle is perfectly suited to bridge two B-sites by a NH3 group. Along the direction of the BX2 plane that does not contain these NH3 bridges, an X-site double layer with only intermolecular interactions between CH3 units occurs. This leads to an elongated lattice in this direction analogous to layered perovskites in the Ruddlesden–Popper phase.\(^{18−20}\) As such, this structural variant could host even larger organic groups.

The electronic structure of \( (\text{MA})_2\text{SeI} \) is shown in Figure 2a,b. For inverse materials, it can be expected that the electronic structure can be deduced from traditional perovskites, by inverting the contributions at the valence band (VB) and conduction band (CB) edges, which are dominated in conventional perovskites by X-site anions and B-site cations, respectively. Despite the phase change to CaIrO3, this inverted band structure is observed for \( (\text{MA})_2\text{SeI} \), with X-site anion contributions in the CB region and contributions from the B- and A-site anions in the VB region.

In order to estimate the stability of our new materials toward decomposition, we compute the formation energy for the reaction \((\text{MA})_3a^2− \rightarrow (\text{MA})_3\text{a}^− \rightarrow (\text{MA})_3\text{a}^2−/\text{a}^− \), which corresponds to the synthetical route often used for HPs\(^{25}\) (Table 1; see Figures S1 and S2 for details). With respect to this reaction, \( (\text{MA})_3\text{SeI} \) is predicted to be thermodynamically unstable by 0.28 eV/f.u.

The ionic radius for Te2− is essentially identical to that of \( \Gamma^− \). This means that the site preference is unclear and that competing structural phase alternatives to the IHP become more likely. A-site Te2− and, thus, the perovskite structure...
In addition to lattice distortion from the cubic phase (Table 1), IHPs naturally show pronounced B-site off-center displacements due to the uneven binding strength of B-site anions to CH$_3$ and NH$_3$ units. Therefore, we expect IHPs to be polar and therefore, the best suitable halogen to stabilize perovskites is again F on the B-site. The obtained electronic structure for (MA)$_3$FTl differs greatly from structures with chalcogenides. Note that the partially filled valence p shell requires spin-polarized treatment. Calculations including Tl (and Pb below) were carried out fully relativistically including SOC. We obtain a metallic band structure (Figure 3a,b), with Tl 6p states around the Fermi level. SOC leads to splitting of these bands into two $j = 1/2$ and four $j = 3/2$ bands. The lower pair of $j = 3/2$ bands is fractionally occupied by about one electron per f.u., in line with the formal charge of Tl$^{2+}$. Due to SOC and inversion symmetry breaking, doubly degenerate Kramers theorem enforced Weyl points are found at $\Gamma$ and each of the sampled high-symmetry points for this semimetal. In the primitive unit cell, we obtain a nonmagnetic structure, but further stabilization of antiferromagnetic spin

Table 1. Tolerance Factor $t$, Structure Information, Formation Energies $E_{\text{form}}$, and Band Gap $E_g$ for the Investigated (MA)$_3$BA Compounds$^a$

<table>
<thead>
<tr>
<th>system</th>
<th>$t$</th>
<th>structure</th>
<th>V (atom/Å$^3$)</th>
<th>$a_0$ (Å)</th>
<th>$b_0$ (Å)</th>
<th>$c_0$ (Å)</th>
<th>$\alpha$ (deg)</th>
<th>$\beta$ (deg)</th>
<th>$\gamma$ (deg)</th>
<th>$E_g$ (eV)</th>
<th>$E_{\text{form}}$ (eV/f.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MA)$_3$Se</td>
<td>0.75</td>
<td>CaIrO$_3$</td>
<td>9.175</td>
<td>7.030</td>
<td>6.931</td>
<td>5.232</td>
<td>94.75</td>
<td>71.89</td>
<td>99.88</td>
<td>3.39</td>
<td>0.28</td>
</tr>
<tr>
<td>(MA)$_3$Te</td>
<td>0.89</td>
<td>P</td>
<td>8.836</td>
<td>5.996</td>
<td>6.460</td>
<td>5.932</td>
<td>91.28</td>
<td>90.28</td>
<td>89.79</td>
<td>3.15</td>
<td>(3.38) −0.71</td>
</tr>
<tr>
<td>(MA)$_3$Pb</td>
<td>0.90</td>
<td>P</td>
<td>8.646</td>
<td>5.839</td>
<td>6.481</td>
<td>5.951</td>
<td>92.77</td>
<td>91.51</td>
<td>91.23</td>
<td>metallic</td>
<td>0.90</td>
</tr>
<tr>
<td>(MA)$_3$AuTe</td>
<td>0.91</td>
<td>P</td>
<td>8.633</td>
<td>5.855</td>
<td>6.453</td>
<td>5.944</td>
<td>91.76</td>
<td>90.76</td>
<td>90.38</td>
<td>0.07</td>
<td>(0.10) −0.58</td>
</tr>
<tr>
<td>(MA)$_3$Te</td>
<td>0.76</td>
<td>CaIrO$_3'$</td>
<td>8.671</td>
<td>6.332</td>
<td>6.274</td>
<td>5.916</td>
<td>85.47</td>
<td>77.22</td>
<td>79.90</td>
<td>2.35</td>
<td>(2.42) 0.21</td>
</tr>
</tbody>
</table>

$^a$For cases with an indirect band gap, the direct band gap $E_g^\text{dir}$ is given in parentheses. P = perovskite. ‘$-$’ = distorted structure.
structures could occur in larger cells. In its present structure, (MA)₃FTI has a high formation energy of 0.9 eV/f.u., i.e., fabrication might require metastable phase engineering.³⁴

We further explore this concept and try to open a small gap by adding another electron, i.e., we substitute TI with Pb. Once again, the tolerance factor is optimal with fluorine on the B-site. The band topology of (MA)₃FPb (Figure 3c,d) is identical to the TI case, but due to the additional electron, a small gap of 0.07 eV is successfully opened between the four j = 3/2 bands. In contrast to TI, Pb leads to a thermodynamically favorable structure (−0.58 eV/f.u. formation energy), demonstrating the feasibility of small band gap IHPs.

Finally, we investigate the possibility to employ transition-metal anions, with the idea being to fill the valence d shell in order to form a ¹⁻ or a ²⁻ anions, by employing group 10 or 11 elements. The ionic radii of these transition metals are of intermediate size, and a perfect candidate that favors the perovskite structure is hard to find. Nevertheless, we show by the example of Au¹⁻ that this route is promising in order to obtain moderate band gaps. On the basis of ionic radii, Au¹⁻ favors the B-site in conjunction with Te (t = 0.76), whereas Se is even less suitable, giving almost identical tolerance factors of about 0.70 on either site. The small tolerance factor of (MA)₃AuTe leads to a strong distortion of the Au(MA)₆ octahedrons in the CaIrO₃ phase, which is more stable than an undistorted structure, the perovskite phase, or compounds with exchanged ion positions.

The electronic structure of this most stable corner- and edge-sharing structure is shown in Figure 3e,f. Gold B-site contributions are observed at both the VB and the CB edge. These contributions arise from the filled valence 6s and 5d orbitals as well as the empty 6p orbitals, confirming the formation of Au¹⁻. With gold anions contributing to CB and VB, the band gap is significantly reduced compared to chalcogenide halide IHPs to 2.35 eV. However, due to the intermediate ionic radii, promising compounds that favor a perovskite structure are not easy to find and require further tuning.

We introduce IHPs as a new materials class. Tolerance factors are used to guide our compositional search because they provide a valuable estimate for the stability of the perovskite structure, with a threshold value of t ≥ 0.76. For smaller values, a mixed corner- and edge-sharing phase occurs, which can be further explored in conjunction with larger organic X-site cations. For all halogen compounds, pairing heavier elements with small halogens, i.e., exchanging anion sites, successfully stabilizes the perovskite structure. Chalcogenide halides form large band gap semiconductors, with a band gap tunable by the ion composition. Electronically, the expected inversion of band character compared to that of conventional perovskites is observed. By changing the ion composition, a variety of electronic behavior is observed, ranging from metallic systems, over systems with very small band gaps due to SOC, to semiconductors. The inclusion of transition metals seems to be a promising route for systems with photovoltaic potential, whereas others show interesting topological behavior. We predict that the suggested compounds can be thermodynamically stable against decomposition and demonstrate the absence of soft phonons for one case, [(MA)₃FTe]. IHPs show great variety with respect to ion composition as well as electronic properties. Furthermore, IHPs have technologically interesting polar phases with large polarization, and we hope that our study triggers research efforts to further explore this new modification of functional perovskite materials. Due to the changed bonding site of the organic anion, the proposed IHPs could also be superior in terms of stability compared to traditional HPs.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.7b00966.

Details on the computational methods, ionic radii, and employed reference states for the evaluation of formation energies and phonon band structure for (MA)₃FTe (PDF)

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The authors declare no competing financial interest.

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