- Supporting information -

Influence of Bi doping on physical properties of lead halide perovskites: a comparative first-principles study between CsPbI$_3$ and CsPbBr$_3$

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Table S1

The cell-size dependence of the formation energy of Bi$_{Pb}^{1+}$ in α-CsPbI$_3$ using the PBE without the SOC effect. The value is presented as the relative value ($\Delta E^f$) relative to the one using a 5x5x5 supercell.

<table>
<thead>
<tr>
<th>Supercell size</th>
<th>$\Delta E^f$ (Bi$_{Pb}^{1+}$) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3x3x3</td>
<td>-0.0745</td>
</tr>
<tr>
<td>4x4x4</td>
<td>0.0006</td>
</tr>
<tr>
<td>5x5x5</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Fig S1. Stability regions of different compounds with respect to \( X \) and Pb chemical potentials in CsPbX\(_3\) [\( X=\text{I for (a) and Br for (b)} \). Chemical potentials of each element referenced to the energy of their own stable phases are listed in Table S2 for three representative points A (\( X \)-poor), B (intermediate), and C (\( X \)-rich).
Table S2

The chemical potentials of each element in eV depending on the growth conditions shown in Fig. S1. The values for Bi-rich are used for calculating the formation energy of Bi\textsubscript{Pb}.

<table>
<thead>
<tr>
<th></th>
<th>(\mu\textsubscript{Cs})</th>
<th>(\mu\textsubscript{Pb})</th>
<th>(\mu\textsubscript{X})</th>
<th>(\alpha)-CsPb\textsubscript{I} _3</th>
<th>(\delta)-CsPbBr\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-2.72</td>
<td>0.00</td>
<td>-1.16</td>
<td>-2.93</td>
<td>-1.50</td>
</tr>
<tr>
<td>B</td>
<td>-3.30</td>
<td>-1.16</td>
<td>-0.58</td>
<td>-3.54</td>
<td>-1.64</td>
</tr>
<tr>
<td>C</td>
<td>-3.88</td>
<td>-2.32</td>
<td>0.00</td>
<td>-4.16</td>
<td>-3.28</td>
</tr>
<tr>
<td>Bi-rich</td>
<td>-3.21</td>
<td>-1.00</td>
<td>-0.66</td>
<td>-3.50</td>
<td>-1.56</td>
</tr>
</tbody>
</table>

A: \(\mu\textsubscript{Cs}\) - 2.72, \(\mu\textsubscript{Pb}\) - 0.00, \(\mu\textsubscript{X}\) - 1.16
B: \(\mu\textsubscript{Cs}\) - 3.30, \(\mu\textsubscript{Pb}\) - 1.16, \(\mu\textsubscript{X}\) - 0.58
C: \(\mu\textsubscript{Cs}\) - 3.88, \(\mu\textsubscript{Pb}\) - 2.32, \(\mu\textsubscript{X}\) - 0.00
Bi-rich: \(\mu\textsubscript{Cs}\) - 3.21, \(\mu\textsubscript{Pb}\) - 1.00, \(\mu\textsubscript{X}\) - 0.66
Calculation of the equilibrium Fermi level

For the calculation of the equilibrium Fermi level (or the equilibrium concentration of free carriers, the native acceptors, and ionized Bi\textsubscript{Pb}) at a given temperature, we applied the charge neutrality condition which is given by \( n = [\text{Bi}_{\text{Pb}}^{1+}] \) if the compensation by the native acceptors is negligible. Using Eqs. 4 and 5 in the text, this neutrality condition can be expressed by \( N_C \exp \left( \frac{E_F - \text{CBM}}{kT} \right) = \frac{[\text{Bi}_{\text{Pb}}^{\text{tot}}]}{1 + 2\exp \left( \frac{E_F - \epsilon (1 + 2)}{kT} \right)} \). The consideration of effects of the native acceptors modifies the neutrality condition as \( n + [V_{\text{Cs}}^{1-}] + 2 \times [V_{\text{Pb}}^{2-}] + [I_{\text{i}}^{1-}] = [\text{Bi}_{\text{Pb}}^{1+}] \), which can be expressed as

\[
N_C \exp \left( \frac{E_F - \text{CBM}}{kT} \right) + N_{\text{Cs}} \exp \left\{ - \frac{E_f (V_{\text{Cs}})}{kT} \right\} + 2 \times N_{\text{Pb}} \exp \left\{ - \frac{E_f (V_{\text{Pb}})}{kT} \right\} + N_{\text{Cs}} \exp \left\{ - \frac{E_f (V_{\text{Cs}})}{kT} \right\} = \frac{[\text{Bi}_{\text{Pb}}^{\text{tot}}]}{1 + 2\exp \left( \frac{E_F - \epsilon (1 + 2)}{kT} \right)}
\]

by using Eqs. 4-6. For a given \([\text{Bi}_{\text{Pb}}^{\text{tot}}]\), we determined the equilibrium Fermi level by evaluating \( E_F \) to solve the above neutrality equations. For instance, neglecting the compensation by native acceptors, the equilibrium Fermi level for CsPbBr\textsubscript{3} including \([\text{Bi}_{\text{Pb}}^{\text{tot}}]=10^{20} \text{ cm}^{-3}\) is CBM−0.25 eV, which leads to the equal concentration (\( \sim 10^{14} \text{ cm}^{-3} \)) of free electrons and \([\text{Bi}_{\text{Pb}}^{1+}]\).