- 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 $\mathrm{Bi}_{\mathrm{Pb}}^{1+}$ in α-$CsPbI_3$ using the PBE without the SOC effect. The value is presented as the relative value (ΔE^f) relative to the one using a 5×5×5 supercell.

Supercell size	ΔE^f ($\mathrm{Bi}_{\mathrm{Pb}}^{1+}$) (eV)
3×3×3	−0.0745
4×4×4	0.0006
5×5×5	0.0

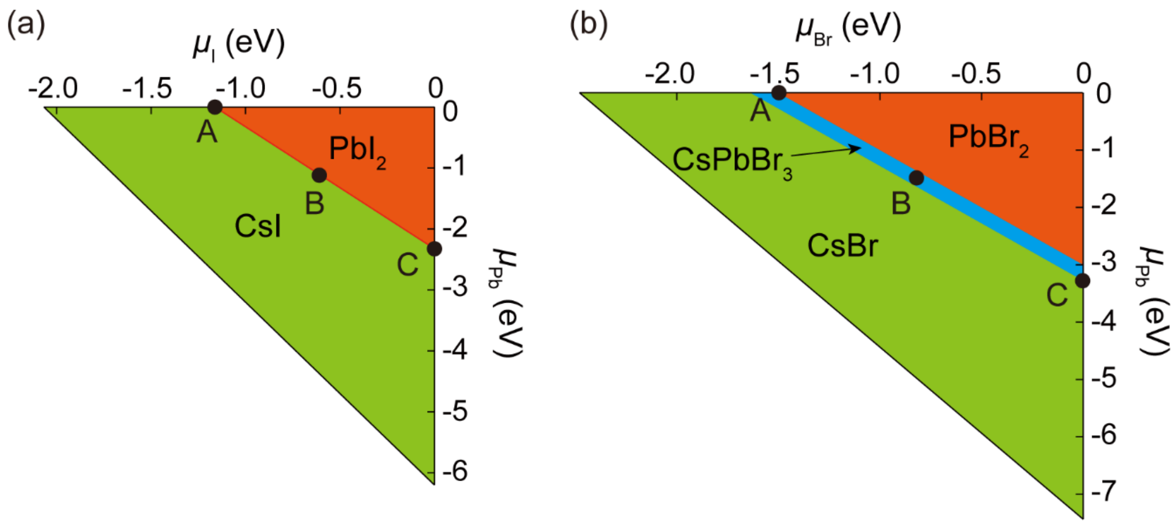

Fig S1. Stability regions of different compounds with respect to *X* and Pb chemical potentials in $CsPbX_3$ [*X*=I for (a) and Br for (b)]. Chemical potentials of each element referenced to the energy of their own stable phases are listed in Table S2 for three representative points A (*X*-poor), B (intermediate), 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_{Pb}.

		α-$CsPbI_3$	δ-$CsPbBr_3$
A	μ_{Cs}	−2.72	−2.93
	μ_{Pb}	0.00	0.00
	μ_X	−1.16	−1.50
B	μ_{Cs}	−3.30	−3.54
	μ_{Pb}	−1.16	−1.64
	μ_X	−0.58	−0.75
C	μ_{Cs}	−3.88	−4.16
	μ_{Pb}	−2.32	−3.28
	μ_X	0.00	0.00
Bi-rich	μ_{Cs}	−3.21	−3.50
	μ_{Pb}	−1.00	−1.56
	μ_X	−0.66	−0.79

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 $\mathrm{Bi_{Pb}}$) at a given temperature, we applied the charge neutrality condition which is given by $n = [\mathrm{Bi}_{\mathrm{Pb}}^{1+}]$ if the compensation by the native acceptors is negligible. Using Eqs. 4 and 5 in the text, this neutrality condition can be expressed by $N_{\mathrm{C}} \exp\left(\frac{E_{\mathrm{F}}-\mathrm{CBM}}{kT}\right) = \frac{[\mathrm{Bi}_{\mathrm{Pb}}^{\mathrm{tot}}]}{1+2\exp\left\{\frac{E_F-\varepsilon(1+/0)}{kT}\right\}}$. The consideration of effects of the native acceptors modifies the neutrality condition as $n + [V_{\mathrm{Cs}}^{1-}] + 2 \times [V_{\mathrm{Pb}}^{2-}] + [\mathrm{I}_{\mathrm{i}}^{1-}] = [\mathrm{Bi}_{\mathrm{Pb}}^{1+}]$, which can be expressed as $N_{\mathrm{C}} \exp\left(\frac{E_{\mathrm{F}}-\mathrm{CBM}}{kT}\right) + N_{\mathrm{Cs}} \exp\left\{-\frac{E^f(V_{\mathrm{Cs}}^{1-})}{kT}\right\} + 2 \times N_{\mathrm{Pb}} \exp\left\{-\frac{E^f(V_{\mathrm{Pb}}^{2-})}{kT}\right\} + N_{\mathrm{Cs}} \exp\left\{-\frac{E^f(V_{\mathrm{Cs}}^{1-})}{kT}\right\} = \frac{[\mathrm{Bi}_{\mathrm{Pb}}^{\mathrm{tot}}]}{1+2\exp\left\{\frac{E_F-\varepsilon(1+/0)}{kT}\right\}}$ by using Eqs. 4-6. For a given $[\mathrm{Bi}_{\mathrm{Pb}}^{\mathrm{tot}}]$, 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 $\mathrm{CsPbBr_3}$ including $[\mathrm{Bi}_{\mathrm{Pb}}^{\mathrm{tot}}]=10^{20}$ $\mathrm{cm^{-3}}$ is CBM−0.25 eV, which leads to the equal concentration (~10^{14} $\mathrm{cm^{-3}}$) of free electrons and $[\mathrm{Bi}_{\mathrm{Pb}}^{1+}]$.