Supplementary Information

Enhanced stability of triple-halide perovskites $CsPbI_{3-x-y}Br_xCl_y$ (x and y = 0 - 0.024): Understanding the role of Cl doping from ab initio calculations

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Table S1. Lattice parameters and volume of the supercell for triple-halide perovskite configurations (C) listed in Fig. 1 (main text) along with the enthalpy of mixing, ΔU (eV/supercell) at 0K, w.r.t. pure $CsPbI_3$, $CsPbBr_3$, and $CsPbCl_3$; and the formation energy, ΔE_f (eV/supercell). Values with spin-orbit coupling are given within parentheses. The distance between the dopants is shown by the variable D with subscripts, i.e. D_{11} represents dopants within one octahedron, D_{12} shows dopants in the nearest neighbor octahedra, and D_{13}, for dopants in the next nearest neighbor octahedra.

C	Lattice parameters	Volume (Å^3) D (Å)	ΔU	ΔE_f
$CsPbI_3$ (3x3x3)	a = b = c = 19.135 Å α = β = γ = 90.00°	7006.25		0.135 (-0.675)
A1	a = 18.882 Å, b = 18.992 Å, c = 18.913 Å α = 90.00°, β = 89.45°, γ = 90.00°	6782.33 D_{11} = 3.798	-1.058 (-0.943)	-1.215 (-1.755)
A2	a = 18.988 Å, b = 18.818 Å, c = 18.976 Å α = 90.40°, β = 90.00°, γ = 90.00°	6780.43 D_{12} = 8.218	-1.036 (-0.922)	-1.215 (-1.755)
A3	a = 18.975 Å, b = 18.987 Å, c = 18.821 Å α = 90.00°, β = 89.59°, γ = 90.00°	6780.80 D_{12} = 8.217	-1.029 (-0.916)	-1.080 (-1.755)
A4	a = 18.869 Å, b = 19.000 Å, c = 18.926 Å α = 90.00°, β = 90.00°, γ = 90.03°	6785.18 D_{13} =11.764	-0.884 (-0.811)	-0.945 (-1.620)
A5	a = 19.003 Å, b = 18.877 Å, c = 18.926 Å α = 90.00°, β = 90.00°, γ = 90.02°	6789.13 D_{13}= 11.769	-0.883 (-0.809)	-0.945 (-1.620)
A6	a = 18.787 Å, b = 19.011 Å, c = 19.011 Å α = 89.81°, β = 90.19°, γ = 89.81°	6789.96 D_{12}=10.452	-0.840 (-0.740)	-0.945 (-1.620)
A7	a = 18.877 Å, b = 18.997 Å, c = 18.997 Å α = 90.51°, β = 90.00°, γ = 90.00°	6812.45 D_{12}= 9.022	-0.759 (-0.671)	-0.810 (-1.485)
A8	a = 18.872 Å, b = 19.018 Å, c = 18.923 Å α = 90.00°, β = 90.00°, γ = 90.00°	6791.61 D_{12}= 10.161	-0.751 (-0.675)	-0.810 (-1.485)
A9	a = 18.798 Å, b = 19.014 Å, c = 19.014 Å α = 90.00°, β = 90.00°, γ = 90.00°	6796.08 D_{11} = 5.994	-0.695 (-0.606)	-0.810 (-1.485)
A10	a = 18.903 Å, b = 19.031 Å, c = 18.946 Å α = 90.00°, β = 90.00°, γ = 90.00°	6815.69 D_{13}= 14.638	-0.631 (-0.534)	-0.675 (-1.350)
A11	a = 19.026Å, b = 19.026 Å, c = 18.839 Å α = 90.40°, β = 90.00°, γ = 89.81°	6819.51 D_{12}= 8.638	-0.479 (-0.409)	-0.540 (-1.215)
A12	a = 19.028 Å, b = 19.028 Å, c = 18.841 Å α = 90.00°, β = 90.00°, γ = 89.85°	6821.66 D_{13} = 8.689	-0.450 (-0.383)	-0.540 (-1.215)
A13	a = 19.042 Å, b = 18.999 Å, c = 18.852 Å	6820.26	-0.417	-0.540

	$\alpha = 90.00^o$, $\beta = 90.00^o$, $\gamma = 90.00^o$	D_{12} =7.704	(-0.361)	(-1.215)

Table S2. Lattice parameters and volume of the supercell for different configurations (C) of triple halide perovskites having stoichiometry $Cs_{27}Pb_{27}I_{77}Br_2Cl_2$ (see Fig. 3 in main text and Fig. S1) along with the enthalpy of mixing, ΔU (eV/supercell) w.r.t. pure halide perovskites at 0K and the formation energy, ΔE_f (eV/supercell). The numbers in brackets are with spin-orbit coupling.

C	Lattice parameters	Volume (Å^3)	ΔU	ΔE_f
$CsPbI_3$ (3x3x3)	a = b = c = 19.135 Å, $\alpha = \beta = \gamma = 90.00^o$	7006.25		
B1	a = 18.861 Å, b = 18.883 Å, c =18.853 Å $\alpha = 89.58^o$, $\beta = 89.98^o$, $\gamma = 89.98^o$	6714.54	-1.248 (-1.106)	-1.620 (-2.160)
B2	a = 18.989 Å, b = 18.807 Å, c =18.823 Å $\alpha = 90.17^o$, $\beta = 90.10^o$, $\gamma = 89.90^o$	6722.19	-1.196 (-1.061)	-1.485 (-2.160)
B3	a = 18.935 Å, b = 18.850 Å, c =18.823 Å $\alpha = 90.01^o$, $\beta = 89.81^o$, $\gamma = 89.80^o$	6718.40	-1.173 (-1.042)	-1.485 (-2.160)
B4	a = 18.930 Å, b = 18.941 Å, c =18.722 Å $\alpha = 89.94^o$, $\beta = 90.08^o$, $\gamma = 90.07^o$	6712.83	-1.164 (-1.034)	-1.485 (-2.160)
B5	a = 18.817 Å, b = 18.992 Å, c =18.848 Å $\alpha = 90.00^o$, $\beta = 89.92^o$, $\gamma = 90.00^o$	6735.76	-1.135 (-1.005)	-1.485 (-2.160)
B6	a = 18.918 Å, b = 18.887 Å, c =18.841 Å $\alpha = 89.85^o$, $\beta = 90.17^o$, $\gamma = 90.48^o$	6731.97	-1.127 (-1.004)	-1.485 (-2.160)
B7	a = 18.986 Å, b = 18.939Å, c =18.717 Å $\alpha = 89.45^o$, $\beta = 90.14^o$, $\gamma = 89.97^o$	6730.18	-1.076 (-0.957)	-1.350 (-2.025)
B8	a = 18.874 Å, b = 18.852 Å, c =18.912 Å $\alpha = 90.14^o$, $\beta = 90.13^o$, $\gamma = 90.44^o$	6729.130	-1.063 (-0.946)	-1.350 (-2.025)
B9	a = 18.994 Å, b = 18.719Å, C = 18.936 Å $\alpha = 90.19^o$, $\beta = 90.28^o$, $\gamma = 90.26^o$	6732.67	-1.025 (-0.905)	-1.350 (-2.025)
B10	a = 18.858 Å, b = 18.999Å, C=18.835 Å $\alpha = 90.00^o$, $\beta = 89.76^o$, $\gamma = 90.00^o$	6748.26	-0.887 (-0.876)	-1.215 (-1.890)
B11	a = 18.992 Å, b = 18.818Å, c =18.900 Å $\alpha = 90.00^o$, $\beta = 89.47^o$, $\gamma = 90.00^o$	6754.700	-0.879 (-0.771)	-1.215 (-1.890)
B12	a = 18.817 Å, b = 18.992 Å, c =18.848 Å $\alpha = 90.00^o$, $\beta = 89.92^o$, $\gamma = 90.00^o$	6735.76	-0.834 (-0.731)	-1.215 (-1.890)
B13	a = 19.008 Å, b = 18.867 Å, c =18.867 Å $\alpha = 90.39^o$, $\beta = 90.15^o$, $\gamma = 90.15^o$	6766.16	-0.823 (-0.722)	-1.215 (-1.890)
B14	a = 19.015Å, b = 19.015Å, c =18.644 Å $\alpha = 89.86^o$, $\beta = 89.86^o$, $\gamma = 90.16^o$	6741.12	-0.795 (-0.695)	-1.080 (-1.755)
B15	a = 19.021 Å, b = 18.642 Å, c =19.021 Å $\alpha = 90.17^o$, $\beta = 89.77^o$, $\gamma = 89.83^o$	6744.65	-0.740 (-0.641)	-1.080 (-1.755)
B16	a = 18.907 Å, b = 18.907 Å, c =18.926 Å $\alpha = 90.00^o$, $\beta = 90.00^o$, $\gamma = 90.87^o$	6765.57	-0.689 (-0.584)	-0.945 (-1.620)
B17	a = 18.908 Å, b = 18.908 Å, c =18.973 Å $\alpha = 90.00^o$, $\beta = 90.00^o$, $\gamma = 89.34^o$	6783.08	-0.629 (0.557)	-0.945 (-1.620)
B18	a = 18.925 Å, b = 19.017 Å, c =18.848 Å $\alpha = 90.00^o$, $\beta = 90.00^o$, $\gamma = 90.00^o$	6783.33	-0.115 (-0.098)	-0.405 (-1.080)

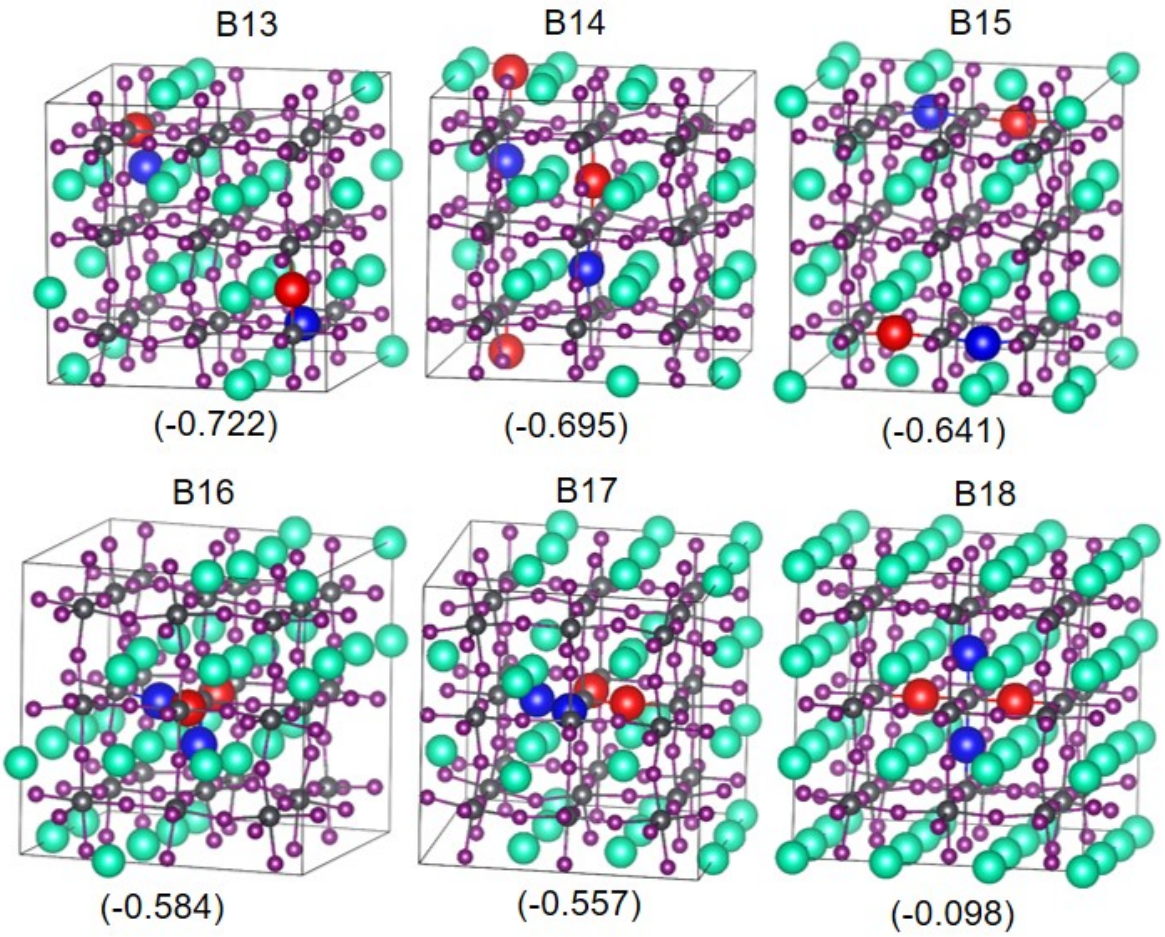

Fig. S1. Relaxed configurations with stoichiometry $Cs_{27}Pb_{27}I_{77}Br_2Cl_2$ when two Br and two Cl are doped at iodine sites. These configurations are in addition to the twelve configurations presented in Fig. 3 in the main text. The ΔU (eV/supercell) values including spin-orbit coupling are listed in parenthesis. Cs, Pb, I, Br, and Cl atoms are shown in light green, grey, purple, red, and blue colors, respectively. The bigger balls are used to represent Br and Cl atoms for clarity.

Calculation of configurational entropy

For a binary solid solution A_sB_t ($t = 1 - s$), the configurational entropy (ΔS_{conf}) is given[1] as:

$$\Delta S_{conf} = -(s \ln s + t \ln t) \quad (1)$$

Where R is the universal gas constant while s and t are atomic fractions of A and B species, respectively. In the case of halide perovskites, experimentally it has been well-studied that Br and/or Cl occupy the iodide sites. Therefore, for this ternary halide system, we calculated the configurational entropy considering only the halide sites. In this case the configurational entropy is given by

$$\Delta S_{conf} = -R[s \ln s + t \ln t + (1-s-t) \ln(1-s-t)]. \quad (2)$$

Here, *s*, *t*, and (1-*s*-*t*) are the atomic fractions of Cl, Br, and I at the halide sites, respectively. Therefore, for the doping of one Cl and one Br ($Cs_{27}Pb_{27}I_{79}BrCl$), the configurational entropy is

$$\Delta S_{conf} = -R\left[\frac{1}{81}ln\left(\frac{1}{81}\right) + \frac{1}{81}ln\left(\frac{1}{81}\right) + \frac{79}{81}ln\left(\frac{79}{81}\right)\right] \quad (3)$$

$$= - R\ (-0.13289)$$
$$= 0.133\ R$$
$$= 1.145 \cdot 10^{-5}\ eVK^{-1}halide^{-1} \qquad \text{where } R = 8.63 \times 10^{-5}\ eVK^{-1}atom^{-1}$$

Further, ΔS_{conf} slightly increases with the increase in the doping concentration for the case of two Cl and two Br ($Cs_{27}Pb_{27}I_{77}Br_2Cl_2$). From Eq. [2] we can write:

$$\Delta S_{conf} = -R\left[\frac{2}{81}ln\left(\frac{2}{81}\right) + \frac{2}{81}ln\left(\frac{2}{81}\right) + \frac{77}{81}ln\left(\frac{77}{81}\right)\right]$$

$$= - R\ (-0.2309)$$
$$= 0.230R$$
$$= 1.990 \cdot 10^{-5}\ eVK^{-1}halide^{-1}$$

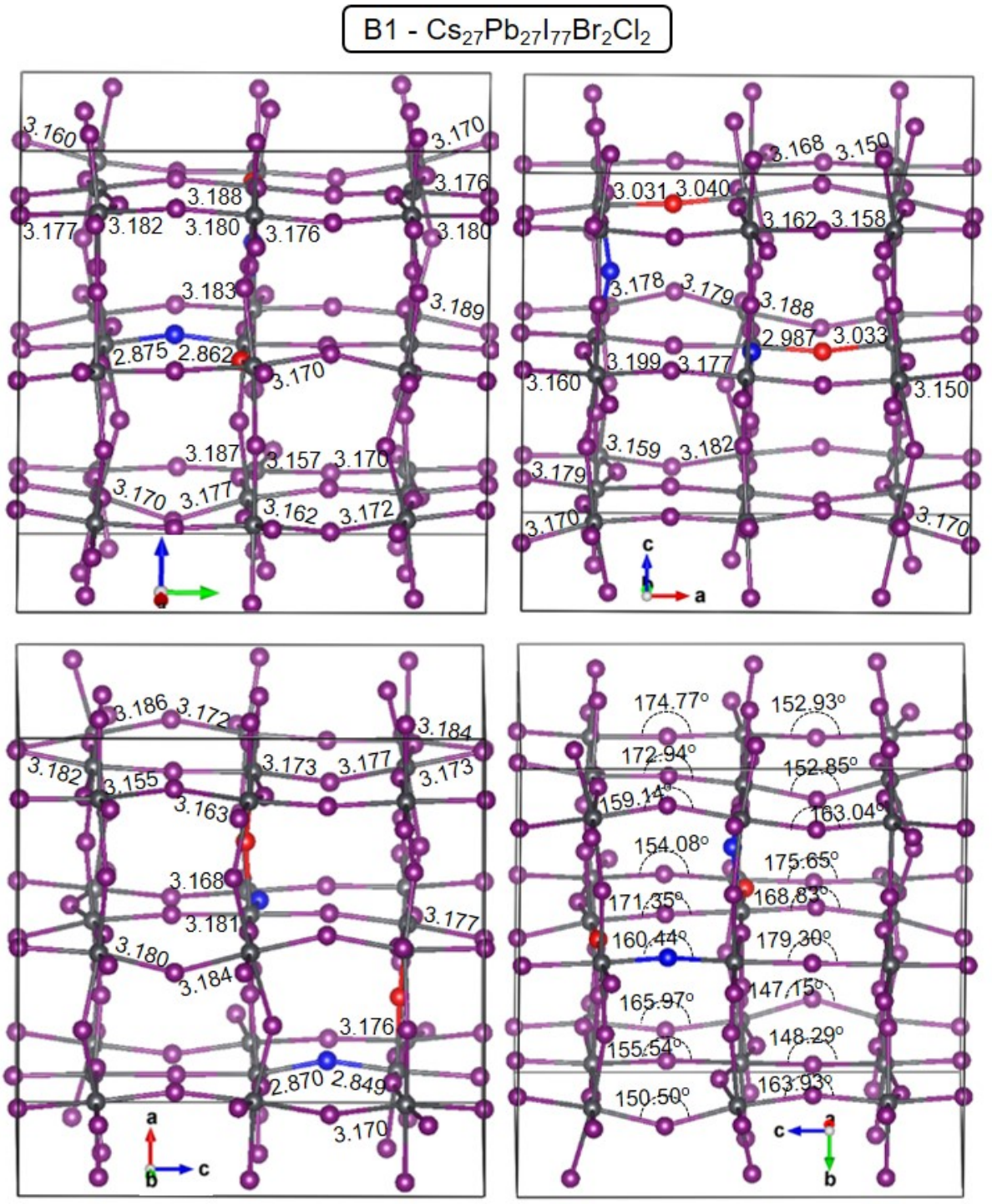

Fig. S2. The optimized atomic structure of B1 configuration (for details see Table S2 and Fig. 3 in the main text), shows the shortened Pb-I bond lengths (presented in three different planes) and tilted PbX_6 octahedra (presented in only one plane with numbers, however distortions are visible in all the shown panels). This is in comparison to $CsPbI_3$ where all Pb-I bond lengths are 3.189 Å with undistorted octahedra (i.e. angle Pb-I-Pb = 180°). Pb, I, Br, and Cl atoms are shown in grey, purple, red, and blue colors, respectively. All cesium atoms are removed for clarity.

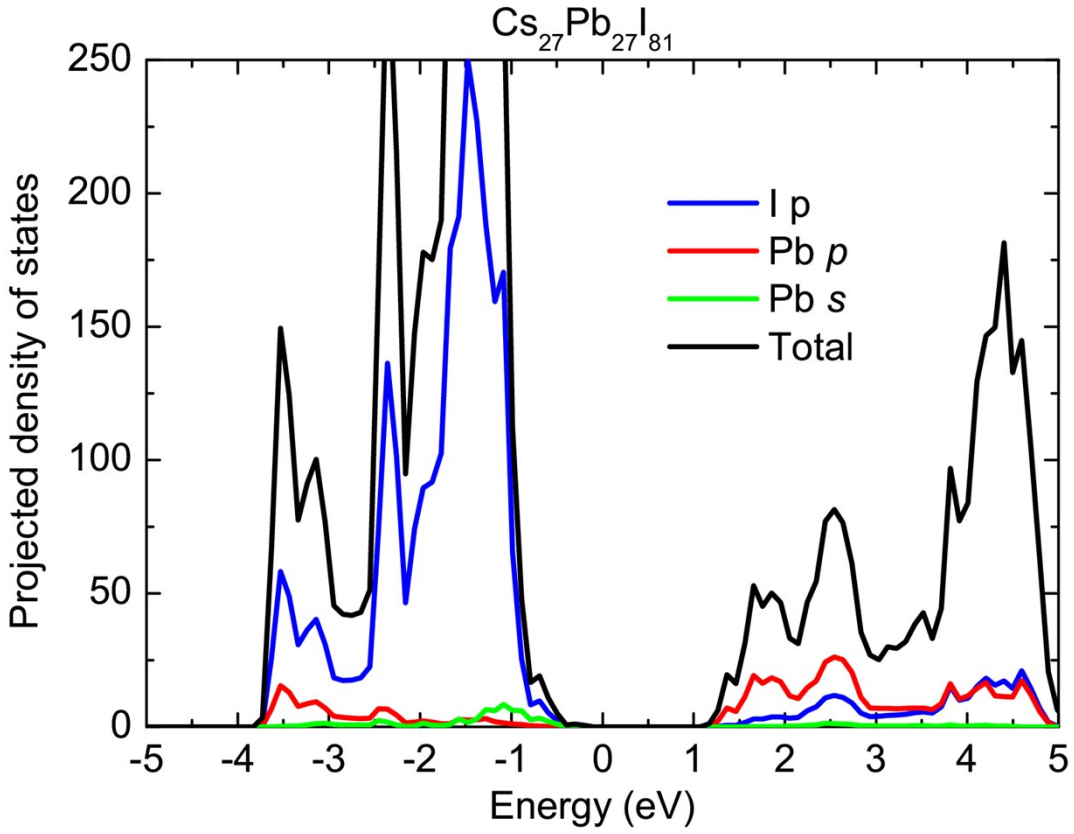

Fig. S3. Projected and total densities of states (states/eV) for a 3x3x3 supercell of $CsPbI_3$.

Reference

[1] Gaskell, D. R. Introduction to the Thermodynamics of Materials, Fifth Edition: Taylor & Francis. (2008).