

Supplementary information

Unexpected bowing band evolution in all-inorganic CsSn_{1-x}Pb_xBr₃ perovskite

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Fig. S1 describes the schematic diagrams of most stable configurations in order to clarify the occupied sites of Sn and Pb atoms, including the $\text{CsSn}_{1-x}\text{Pb}_x\text{Br}_3$ and $\text{MA}_{0.5}\text{Cs}_{0.5}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$ perovskites from $x=0.125$ to $x=0.875$. The position of metal atoms indicates that Sn and Pb atoms occupy dispersedly in the most stable configurations of $\text{CsSn}_{1-x}\text{Pb}_x\text{Br}_3$ (First line). On the contrary, Sn and Pb atoms are inclined to be clustered in the most stable configurations of $\text{MA}_{0.5}\text{Cs}_{0.5}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$ (Second line). Noticeably, all Sn^{2+} cations prefer to get close to MA^+ cation to reduce the local distortion due to its large size. All stable configurations of mixed Cs-MA system show the similar structural properties that Sn atoms are like to stay together near MA^+ cation.

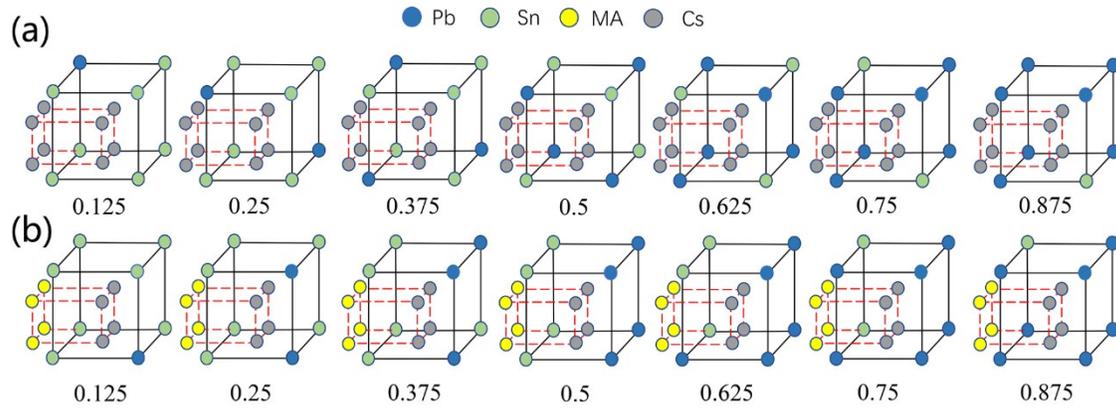


Fig. S1. The most stable configurations obtained by alloying with two metal species for (a) $\text{CsSn}_{1-x}\text{Pb}_x\text{Br}_3$ and (b) $\text{MA}_{0.5}\text{Cs}_{0.5}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$ compositions.

Table S1 and S2 contain total energy, bandgap (GGA, GGA+SOC, ΔSOC) and lattice constant of $\text{MA}_{0.5}\text{Cs}_{0.5}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$ and $\text{CsSn}_{1-x}\text{Pb}_x\text{Br}_3$ configurations. It can be clearly seen that the total energy gradually decreases while x increases in following systems. In reality, this phenomenon is related to the ratio of Pb and Sn in crystal structures. Additionally, the

band gap by GGA+SOC method is a nonlinear trend in $\text{MA}_{0.5}\text{Cs}_{0.5}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$, and the band gaps are lower than pure Sn configuration ($x=0$) when $0.125 \leq x \leq 0.75$, which displays the obvious bowing effect of bandgap following the Vegard's law. Furthermore, when x is equal to 0.25, the decreasing trend of band gap reaches a minimum value (0.626eV). Bowing band evolution is also found in all-inorganic perovskite system ($\text{CsSn}_{1-x}\text{Pb}_x\text{Br}_3$), but its bowing parameter is the smallest. These results show that the MA^+ cation will affect the structural configurations and then influence the electronic properties of bowing band evolution. In addition, the linear variation of lattice constants obeys the Vegard's law in all structures summarized in Table S2.

Table S1. Total energy calculations, band gap of GGA, GGA+SOC, and Δ SOC for selected stable compositions of $\text{MA}_{0.5}\text{Cs}_{0.5}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$ and $\text{CsSn}_{1-x}\text{Pb}_x\text{Br}_3$ configurations. Units are given in eV for total energy and bandgap.

Configuration		Total Energy	GGA	GGA+SOC	Δ SOC
$\text{MA}_{0.5}\text{Cs}_{0.5}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$	$x=0$	-274.051	0.974	0.709	0.265
	$x=0.125$	-274.152	1.057	0.649	0.407
	$x=0.25$	-274.260	1.153	0.626	0.527
	$x=0.375$	-274.377	1.254	0.649	0.605
	$x=0.5$	-274.500	1.352	0.659	0.693
	$x=0.625$	-274.591	1.447	0.671	0.776
	$x=0.75$	-274.689	1.567	0.692	0.875
	$x=0.875$	-274.789	1.725	0.761	0.964
	$x=1$	-274.898	1.913	0.843	1.070
$\text{CsSn}_{1-x}\text{Pb}_x\text{Br}_3$	$x=0$	-126.669	0.638	0.291	0.347
	$x=0.125$	-126.751	0.751	0.283	0.469
	$x=0.25$	-126.830	0.875	0.315	0.560
	$x=0.375$	-126.915	1.007	0.353	0.654
	$x=0.5$	-127.008	1.172	0.433	0.739
	$x=0.625$	-127.094	1.281	0.446	0.835
	$x=0.75$	-127.188	1.419	0.500	0.918
	$x=0.875$	-127.288	1.542	0.542	1.000
	$x=1$	-127.394	1.765	0.672	1.093

Table S2. Relaxed lattice constant for selected compositions of the $\text{MA}_{0.5}\text{Cs}_{0.5}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$ and $\text{CsSn}_{1-x}\text{Pb}_x\text{Br}_3$ configurations. Units are given in Å for lattice constant.

Configuration		Lattice constant average	a	b	c
$\text{MA}_{0.5}\text{Cs}_{0.5}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$	$x=0$	11.952	11.962	11.947	11.948
	$x=0.125$	11.958	11.986	11.945	11.944
	$x=0.25$	11.977	12.009	11.978	11.945
	$x=0.375$	11.987	12.030	11.966	11.966
	$x=0.5$	12.014	12.037	12.001	12.003
	$x=0.625$	12.014	12.043	11.999	11.999
	$x=0.75$	12.027	12.056	12.020	12.006
	$x=0.875$	12.040	12.067	12.026	12.026
	$x=1$	12.058	12.075	12.049	12.050
$\text{CsSn}_{1-x}\text{Pb}_x\text{Br}_3$	$x=0$	11.772	11.772	11.772	11.772
	$x=0.125$	11.800	11.800	11.800	11.800
	$x=0.25$	11.818	11.818	11.818	11.818
	$x=0.375$	11.850	11.850	11.850	11.850
	$x=0.5$	11.874	11.874	11.874	11.874
	$x=0.625$	11.901	11.901	11.901	11.901
	$x=0.75$	11.928	11.928	11.928	11.928
	$x=0.875$	11.951	11.951	11.951	11.951
	$x=1$	11.978	11.978	11.978	11.978

The TDOS and PDOS of Cs-, $\text{MA}_{0.25}\text{Cs}_{0.75}$ - and $\text{MA}_{0.5}\text{Cs}_{0.5}$ - based perovskites with GGA+SOC calculation are shown in Fig. S2-S4. For all structures, the dominant

components for contributing the band edges are very similar. VBM is derived from Sn-5s, Pb-6s, Br-4p orbitals and Sn-5p, Pb-6p orbitals contribute most to the CBM.

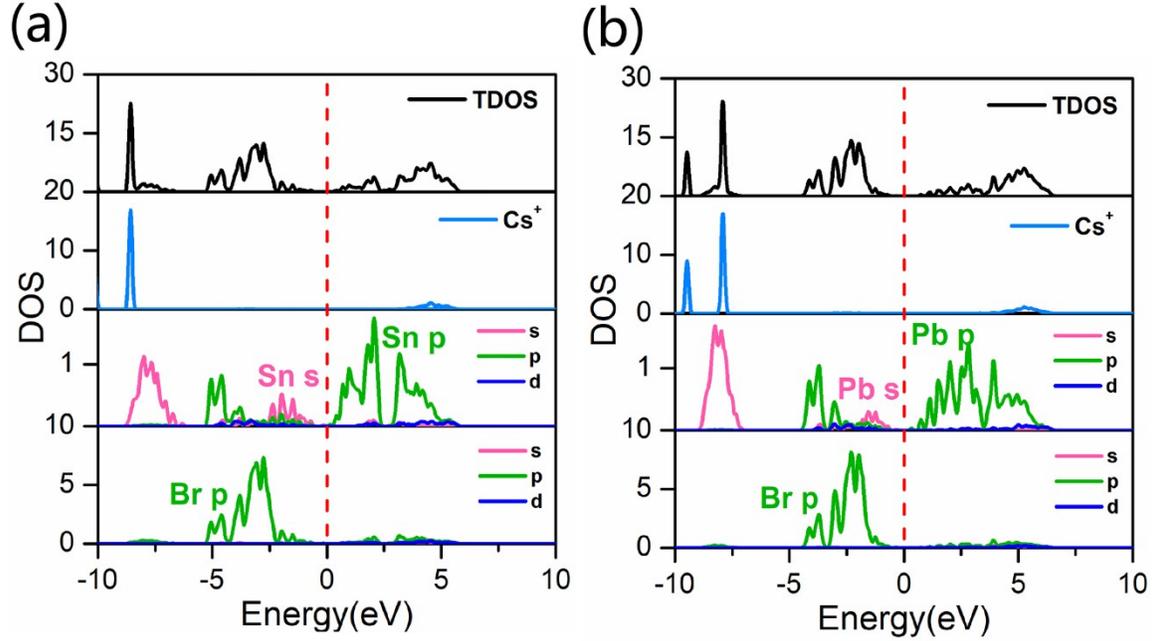


Fig. S2. Total density of state (TDOS) and projected density of states (PDOS) of (a) CsSnBr₃ and (b) CsPbBr₃.

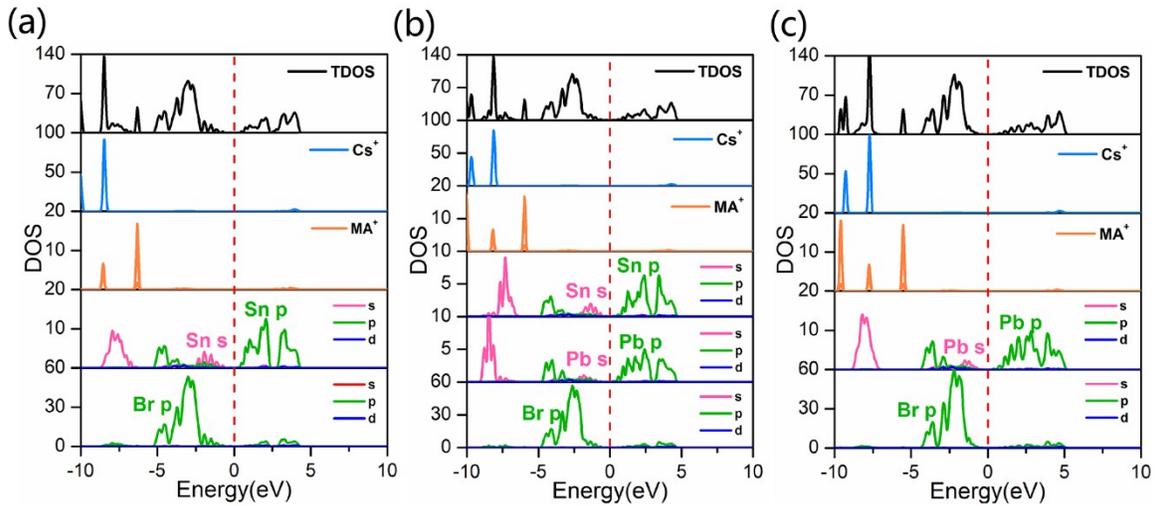


Fig. S3. TDOS and PDOS of (a) MA_{0.25}Cs_{0.75}SnBr₃, (b) MA_{0.25}Cs_{0.75}Sn_{0.5}Pb_{0.5}Br₃ and (c) MA_{0.25}Cs_{0.75}PbBr₃.

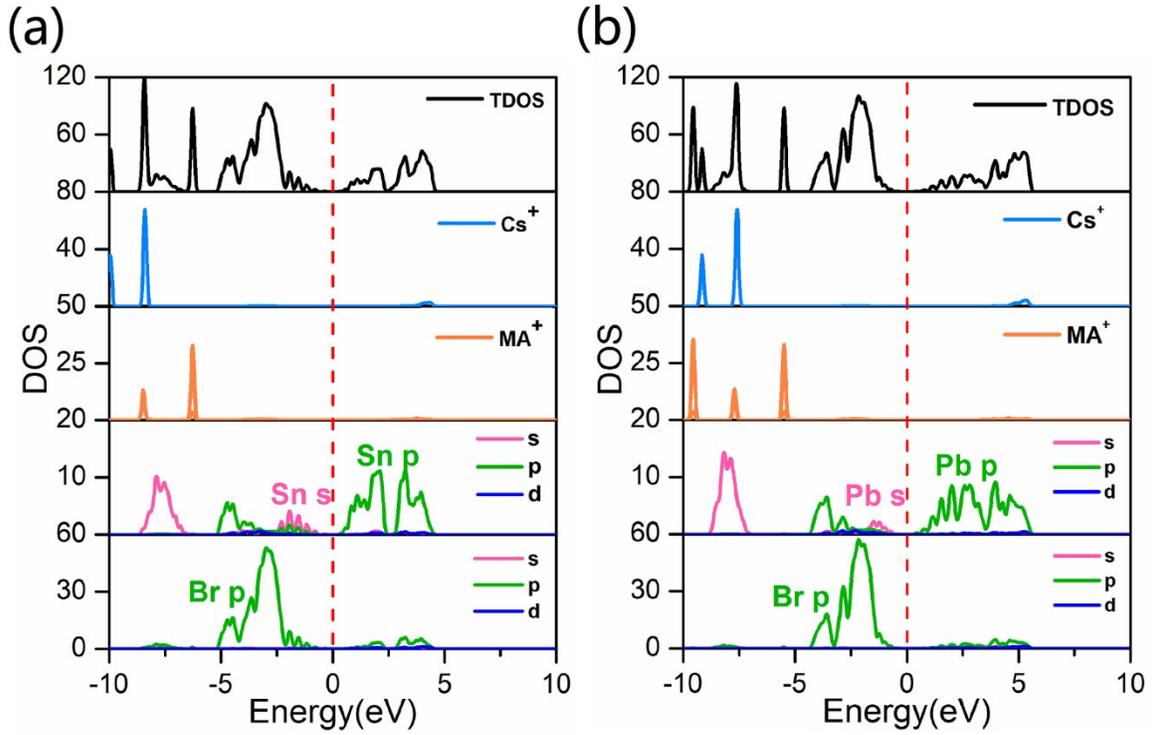


Fig. S4. TDOS and PDOS of (a) $\text{MA}_{0.5}\text{Cs}_{0.5}\text{SnBr}_3$, and (b) $\text{MA}_{0.5}\text{Cs}_{0.5}\text{PbBr}_3$.

The band gaps (GGA, GGA+SOC, ΔSOC) of $\text{MA}_y\text{Cs}_{1-y}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$ ($0.125 \leq y \leq 0.5$) systems are described in Fig. S5-6. It can be clearly seen that the bowing band evolutions are gradually enhanced for pushing the band gap lower than the extreme values (pure Sn and Pb systems) when y increases due to the increase of bowing parameter b values.

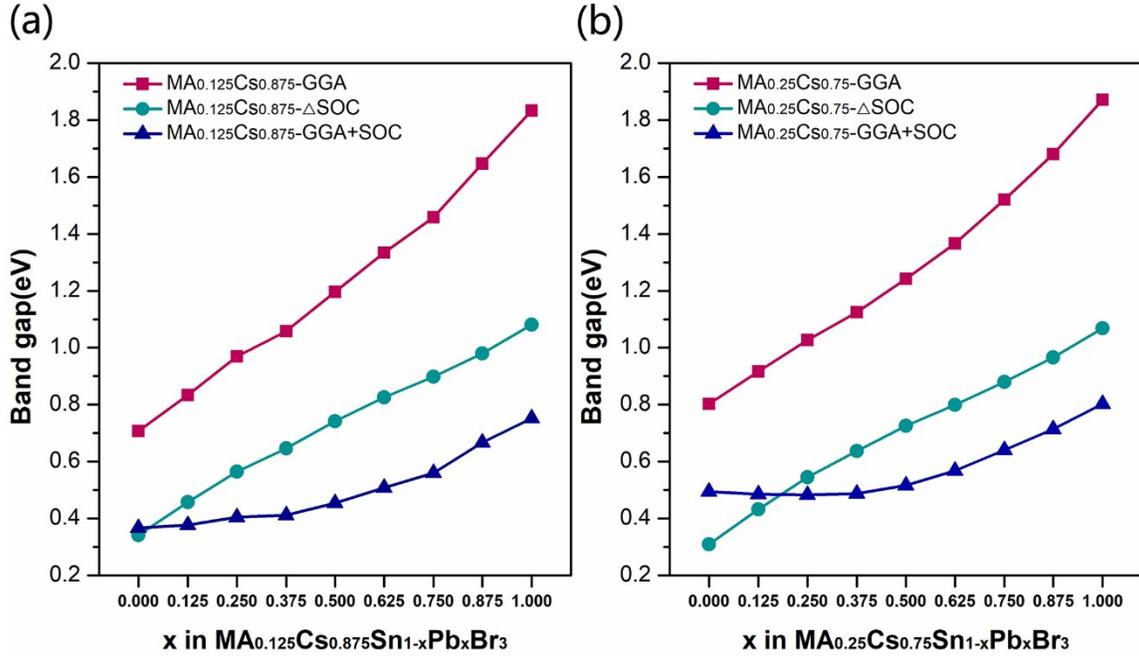


Fig. S5. (a) MA_{0.125}Cs_{0.875}Sn_{1-x}Pb_xBr₃ as a function of composition x , (b) MA_{0.25}Cs_{0.75}Sn_{1-x}Pb_xBr₃ as a function of composition x .

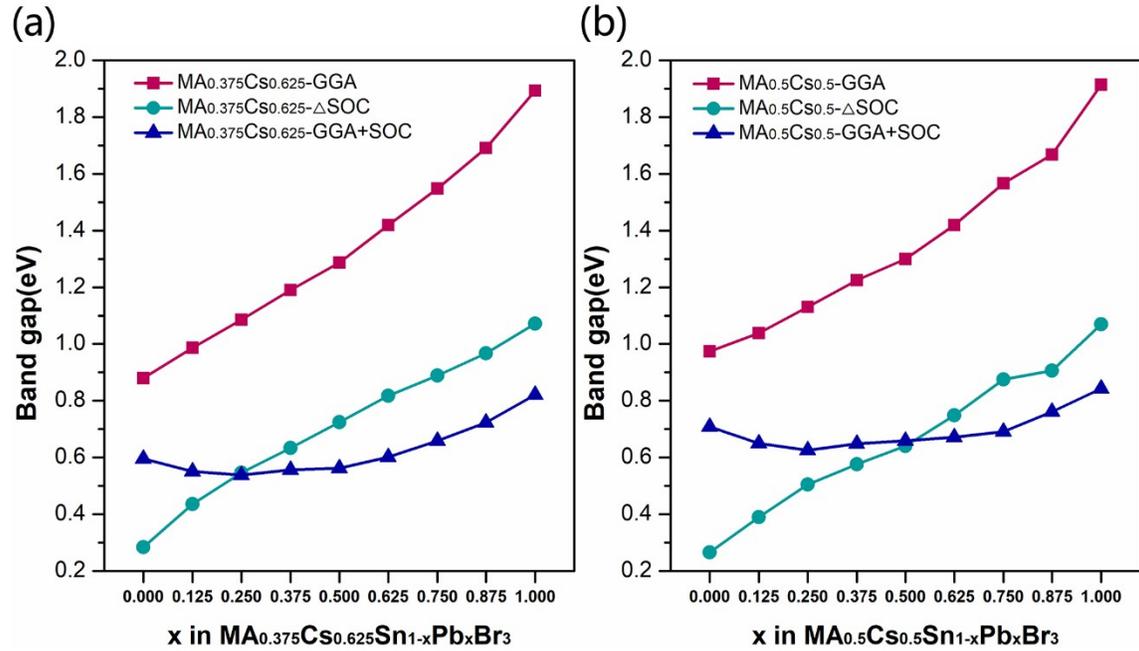


Fig. S6. (a) MA_{0.375}Cs_{0.625}Sn_{1-x}Pb_xBr₃ as a function of composition x , (b) MA_{0.5}Cs_{0.5}Sn_{1-x}Pb_xBr₃ as a function of composition x .

Considering the influence of vdW interaction for the organic MA⁺ cations, we used

semi-local functional optB86b that has been proved to work well in perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ with vdW-DF.¹⁻³ In this work, we also set the same vdW parameter by GGA+SOC method to further calculate the organic perovskite systems. Fig. S7 shows us the curve fittings of $\text{MA}_{0.5}\text{Cs}_{0.5}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$ with vdW-DF and without vdW-DF. Though the absolute values of band gap change, the bowing band evolutions are very similar due to the identical bowing parameters in Table S3. The band gaps considering vdW interaction are slightly larger than that of without considering vdW interaction.

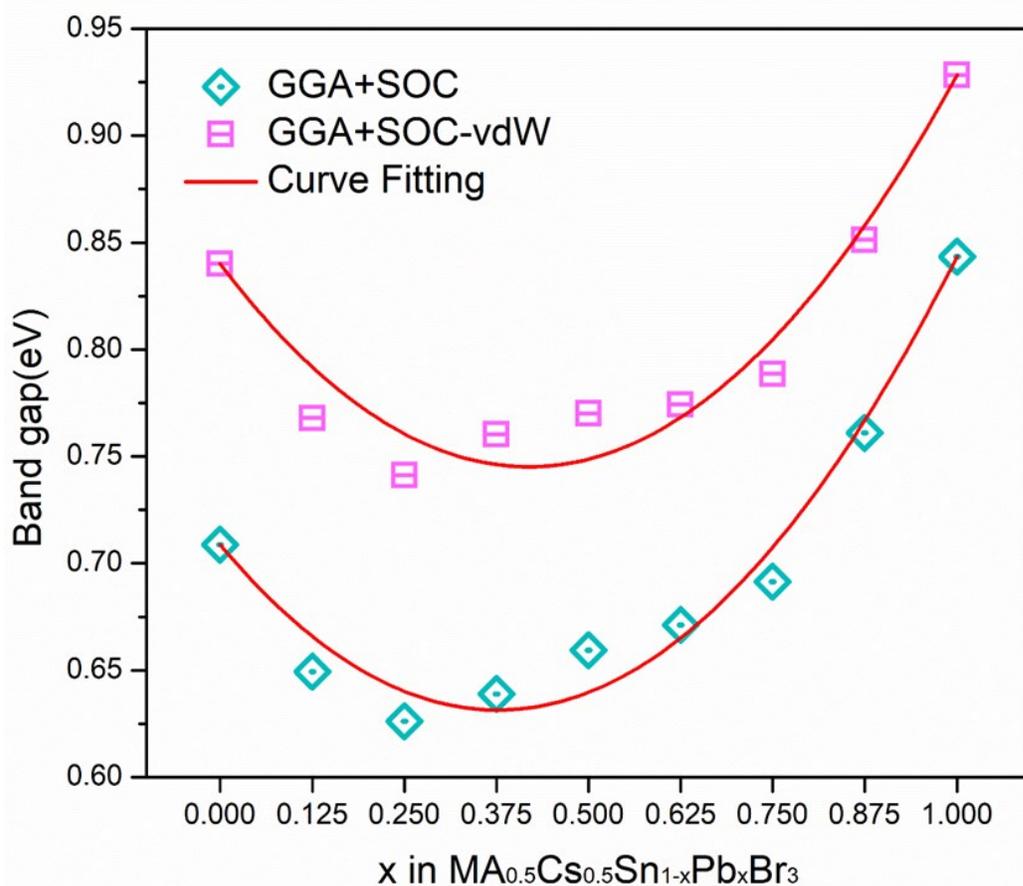


Fig. S7 Calculated band gap evolutions of $\text{MA}_{0.5}\text{Cs}_{0.5}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$ with/without vdW-DF as a function of composition x

Table S3. Fitting quadratic equation and bowing parameter of $\text{MA}_{0.5}\text{Cs}_{0.5}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$ system.

System	Fitting quadratic equation	bowing parameter
$\text{MA}_{0.5}\text{Cs}_{0.5}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$	$E_g = 0.54x^2 - 0.40x + 0.71$	0.54
$\text{MA}_{0.5}\text{Cs}_{0.5}\text{Sn}_{1-x}\text{Pb}_x\text{Br}_3$ - vdW	$E_g = 0.54x^2 - 0.45x + 0.84$	0.54

Reference

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- 2 J. Klimeš, D. R. Bowler and A. Michaelides, *J. Phys. Condens. Matter*, 2009, **22**, 22201.
- 3 J. Klimeš, D. R. Bowler and A. Michaelides, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2011, **83**, 1–13.