

Electronic supplementary information for

Surface energy and surface stability of cesium tin halide perovskites:

A theoretical investigation

Yan-Jin Chen¹, Chunju Hou², Yi Yang,^{1*}

¹ College of Rare Earths and Faculty of Materials, Metallurgy and Chemistry, JiangXi University of Science and Technology, Ganzhou, 341000, China

² School of Science, JiangXi University of Science and Technology, Ganzhou, 341000, China

*Corresponding author, e-mail address: yangyisouth@yeah.net

Formation energy

The formation energies (E_f , eV) of SnX_2 , CsX and CsSnX_3 ($X=\text{Cl, Br, I}$) with respect to element substances are calculated according to the follow formulas:

$$E_{f(\text{SnX}_2)} = E_{\text{SnX}_2} - E_{\text{Sn}} - 2E_X \quad (1)$$

$$E_{f(\text{CsX})} = E_{\text{CsX}} - E_{\text{Cs}} - E_X \quad (2)$$

$$E_{f(\text{CsSnX}_3)} = E_{\text{CsSnX}_3} - E_{\text{Cs}} - E_{\text{Sn}} - 3E_X \quad (3)$$

where E_{SnX_2} , E_{CsX} , E_{CsSnX_3} are the total energies of bulk SnX_2 , CsX , CsSnX_3 respectively. E_{Cs} , E_{Sn} , E_X are the energies (eV per atom) of element substances, i.e., Cs metal, Sn metal and X_2 gas molecule. One exception is I_2 for which a solid structure is used. The E_f of these bulks define the CsX-rich and SnX_2 -rich conditions at which we calculate the E_{surf} values for (100)-CsX and (100)- SnX_2 surfaces (Table 2, Table S2 and Table S3). CsSnX_3 bulk is thermodynamically stable at the chemical potential region between CsX-rich and SnX_2 -rich condition: $-4.30 \leq \Delta\mu_{\text{Cs}} + \Delta\mu_{\text{Cl}} \leq -4.00 \text{ eV}$ for CsSnCl_3 ; $-4.04 \leq \Delta\mu_{\text{Cs}} + \Delta\mu_{\text{Br}} \leq -3.79 \text{ eV}$ for CsSnBr_3 ; and $-3.21 \leq \Delta\mu_{\text{Cs}} + \Delta\mu_{\text{I}} \leq 3.09 \text{ eV}$ for CsSnI_3 . These conditions define the red lines in Fig. 2 of main text. Binary phase CsX or SnX_2 may appear beyond these regions.

Conditions to calculate E_{surf} as a function of $\Delta\mu_X$

In order to show E_{surf} as a function of $\Delta\mu_X$, we calculate E_{surf} at specific chemical potential conditions of Cs. We assume Sn-rich condition (i.e., $\Delta\mu_{\text{Sn}}=0 \text{ eV}$) where Sn source is in equilibrium with CsSnX_3 . For Sn-perovskites, excess Sn may be reached by adding Sn sources such as SnF_2 additive.^{1, 2} Nakamura et al. showed that Sn (0) nanoparticles produced from the reaction of a dihydropyridine derivative with SnF_2 (II) additive can avoid Sn (IV) impurities and improve the efficiency of tin-based solar cells.² Previous works also reported the existence of metal Pb nanoparticles in CsPbBr_3 system.^{3, 4} With $\Delta\mu_{\text{Sn}}=0 \text{ eV}$, we obtain $\Delta\mu_{\text{Cs}} + 3\Delta\mu_{\text{Cl}} = -7.46 \text{ eV}$ for CsSnCl_3 ($\Delta\mu_{\text{Cs}} + 3\Delta\mu_{\text{Br}} = -6.80 \text{ eV}$ for CsSnBr_3 and $\Delta\mu_{\text{Cs}} + 3\Delta\mu_{\text{I}} = -4.67 \text{ eV}$ for CsSnI_3). Combining Sn-rich condition with CsCl-rich and SnCl_2 -rich conditions of stable CsSnCl_3 , we can obtain two typical conditions for Cs: $\Delta\mu_{\text{Cs}} = -2.72 \text{ eV}$ and $\Delta\mu_{\text{Cs}} =$

-2.26 eV for CsSnCl₃. Similarly, $\Delta\mu_{Cs} = -2.66$ eV and $\Delta\mu_{Cs} = -2.29$ eV for CsSnBr₃ and $\Delta\mu_{Cs} = -2.48$ eV and $\Delta\mu_{Cs} = -2.30$ eV for CsSnI₃ can be obtained. The E_{surf} as a function of $\Delta\mu_X$ are calculated at these conditions (Figure 3).

Calculating monolayer exfoliation energy

We calculate the monolayer exfoliation energy (i.e., the energy required in peeling off one-unit-cell CsSnX₃ from CsSnX₃ surface) using slab method.⁵ The calculation models are displayed in Fig. S2. The monolayer exfoliation energy is calculated as the difference in total energies of configurations between Fig. S2(b) and Fig. S2(a). We check the convergence of monolayer exfoliation energy with the thickness of slab by using a CsSnCl₃ slab with eleven layers. The calculated monolayer exfoliation energy is 0.330 J/m², the same as the result from nine-layers model. This indicates the convergence of the quantity. Note that the slab in Fig. S2 is terminated with CsX-layer. We also calculated monolayer exfoliation energy by using SnX₂-terminated nine-layers slab. The calculated results are 0.328, 0.307 and 0.280 J/m² for CsSnCl₃, CsSnBr₃ and CsSnI₃, respectively. These values are very close to those (0.330, 0.307 and 0.281 J/m² in order) obtained from CsX-terminated slabs, providing consistent data for exfoliation energy regardless of the termination of slab.

Table. S1 Formation energies (E_f) of bulk SnX₂, CsX and CsSnX₃ with respect to the element substances. The structures of tin halides (SnCl₂, SnBr₂ and SnI₂) are taken from ref. 6-8 The E_f are also calculated with spin-orbital coupling (E_f -SOC), listed in the third column.

Substances	E_f (eV)	E_f -SOC (eV)
SnCl ₂	-3.16	-3.14
SnBr ₂	-2.76	-2.73
SnI ₂	-1.46	-1.40
CsCl	-4.00	-3.99
CsBr	-3.79	-3.79
CsI	-3.09	-3.05
CsSnCl ₃	-7.46	-7.43
CsSnBr ₃	-6.80	-6.77
CsSnI ₃	-4.67	-4.58

Table S2 Surface energies (E_{surf} , J/m²) of relaxed (100)-CsX and (100)-SnX₂ surfaces calculated with a cutoff of 500 eV and a mesh of 12×12×12 at the CsX-rich (e.g., $\Delta\mu_{\text{Cs}} + \Delta\mu_{\text{Cl}} = -4.00$ eV for CsSnCl₃) and SnX₂-rich conditions ($\Delta\mu_{\text{Cs}} + \Delta\mu_{\text{Cl}} = -4.30$ eV).

Cutoff; mesh		350 eV; 8×8×8		500 eV; 12×12×12	
CsSnX ₃	$\Delta\mu_{\text{Cs}} + \Delta\mu_{\text{X}}$ (eV)	CsX	SnX ₂	CsX	SnX ₂
CsSnCl ₃	-4.00	0.069	0.135	0.070	0.134
	-4.30	0.148	0.055	0.146	0.057
CsSnBr ₃	-3.79	0.059	0.162	0.058	0.162
	-4.04	0.119	0.101	0.119	0.102
CsSnI ₃	-3.09	0.043	0.156	0.045	0.158
	-3.21	0.068	0.130	0.069	0.135

Table S3 Surface energies (E_{surf} , J/m²) of relaxed (100)-CsBr and (100)-SnBr₂ surfaces of CsSnBr₃ calculated without SOC and with SOC at the CsBr-rich (e.g., $\Delta\mu_{\text{Cs}} + \Delta\mu_{\text{Br}} = -3.79$ eV) and SnBr₂-rich conditions ($\Delta\mu_{\text{Cs}} + \Delta\mu_{\text{Br}} = -4.04$ eV).

$\Delta\mu_{\text{Cs}} + \Delta\mu_{\text{Br}}$ (eV)	Without SOC		With SOC	
	CsBr	SnBr ₂	CsBr	SnBr ₂
-3.79	0.059	0.162	0.062	0.160
-4.04	0.119	0.101	0.123	0.100

Table S4 Cleavage energies (E_{cl} , J/m²) of CsSnBr₃ and CsPbBr₃ cutting through its (100), (110), and (111) surfaces. The values of CsPbBr₃ are taken from ref. 9.

E_{cl} CsMBr ₃	(100)	(110) polar	(110) non- polar	(111) polar
CsSnBr ₃	0.355	1.193	0.652	0.964
CsPbBr ₃	0.344	1.407	0.658	1.166

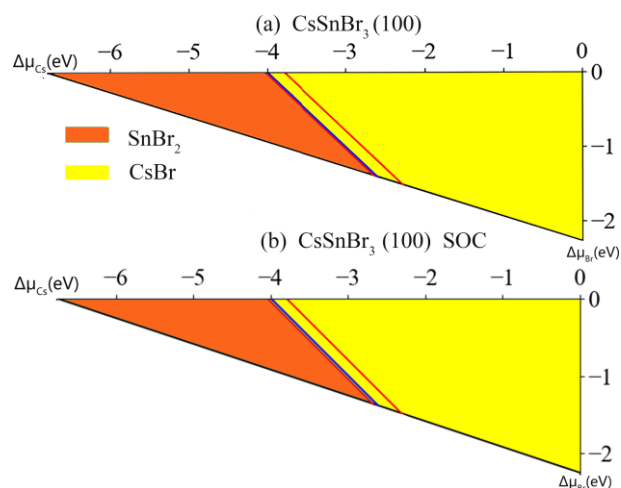


Fig. S1 Calculated phase diagrams of CsSnBr_3 (100) surfaces: (a) without SOC; (b) SOC.

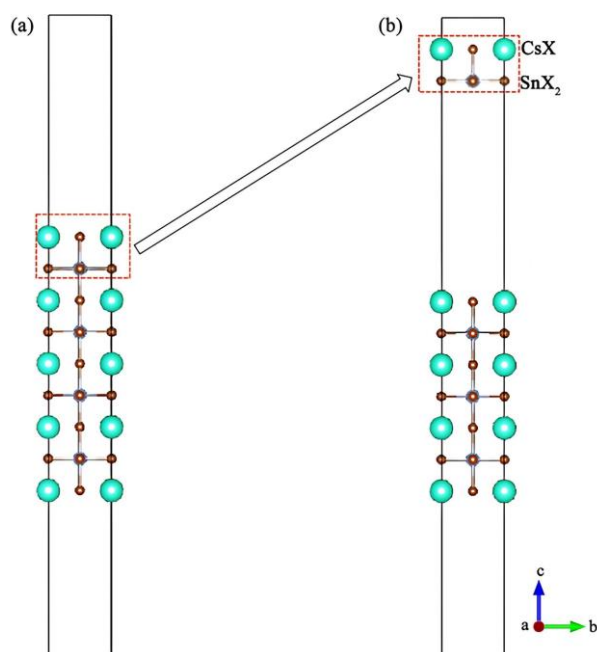


Fig. S2 Calculation models of the monolayer exfoliation energy through (100) plane of CsSnX_3 : (a) a slab with nine atomic layers (4.5-unit cells); (b) the topmost unit cell of the slab being separated. The monolayer exfoliation energy is calculated as the difference in total energies between the configuration (b) and (a). The separated model in (b) remains its split style without further relaxation. The vacuum thicknesses are larger than 15 \AA .

References

1. R. Lin, K. Xiao, Z. Qin, Q. Han, C. Zhang, M. Wei, M. I. Saidaminov, Y. Gao, J. Xu, M. Xiao, A. Li, J. Zhu, E. H. Sargent and H. Tan, *Nat. Energy*, 2019, **4**, 864-873.
2. T. Nakamura, S. Yakumaru, M. A. Truong, K. Kim, J. Liu, S. Hu, K. Otsuka, R. Hashimoto, R. Murdey, T. Sasamori, H. D. Kim, H. Ohkita, T. Handa, Y. Kanemitsu and A. Wakamiya, *Nat. Commun.*, 2020, **11**, 3008.
3. T. Udayabhaskararao, M. Kazes, L. Houben, H. Lin and D. Oron, *Chem. Mater.*, 2017, **29**, 1302-1308.
4. M. Zhang, H. Li, Q. Jing, Z. Lu and P. Wang, *Crystals*, 2017, **8**, 2.
5. J. H. Jung, C. H. Park and J. Ihm, *Nano Lett*, 2018, **18**, 2759-2765.
6. J. M. van den Berg, *Acta Crystallogr.*, 1961, **14**, 1002-1003.
7. P. Ravindran, A. Delin, R. Ahuja, B. Johansson, S. Auluck, J. M. Wills and O. Eriksson, *Phys. Rev. B*, 1997, **56**, 6851-6861.
8. P. Eckold, W. Hugel, R. E. Dinnebier and R. Niewa, *Z. Anorg. Allg. Chem.*, 2015, **641**, 1467-1472.
9. Y. Yang, C. Hou and T. X. Liang, *Phys. Chem. Chem. Phys.*, 2021, **23**, 7145-7152.