Electronic Supplementary Information (ESI) for

Carrier mobilities and band alignments of inorganic perovskites of $CsBX_3$

Weitao Yan[a], Yao Sun[b], Xiaokun Zhao[b], Wen Yang[c], Boyan Li[*b] , Dalong Zhong[b], Feng Lu[a], Wei-Hua Wang[*a]

[a]*Department of Electronic Science and Engineering, and Tianjin Key Laboratory of Efficient Utilization of Solar Energy, Nankai University, Tianjin 300350, China*

[b]*National Institute of Clean-and-Low-Carbon Energy and Beijing Engineering Research Center of Nano-structured Thin Film Solar Cells, Beijing 102211, China*

[c]*Shanxi Key Laboratory of Metal Forming Theory and Technology, School of Material Science and Engineering, Taiyuan University of Science and Technology, Taiyuan 030024, Shanxi, China*

*E-mail: boyan.li.a@chnenergy.com.cn, whwangnk@nankai.edu.cn

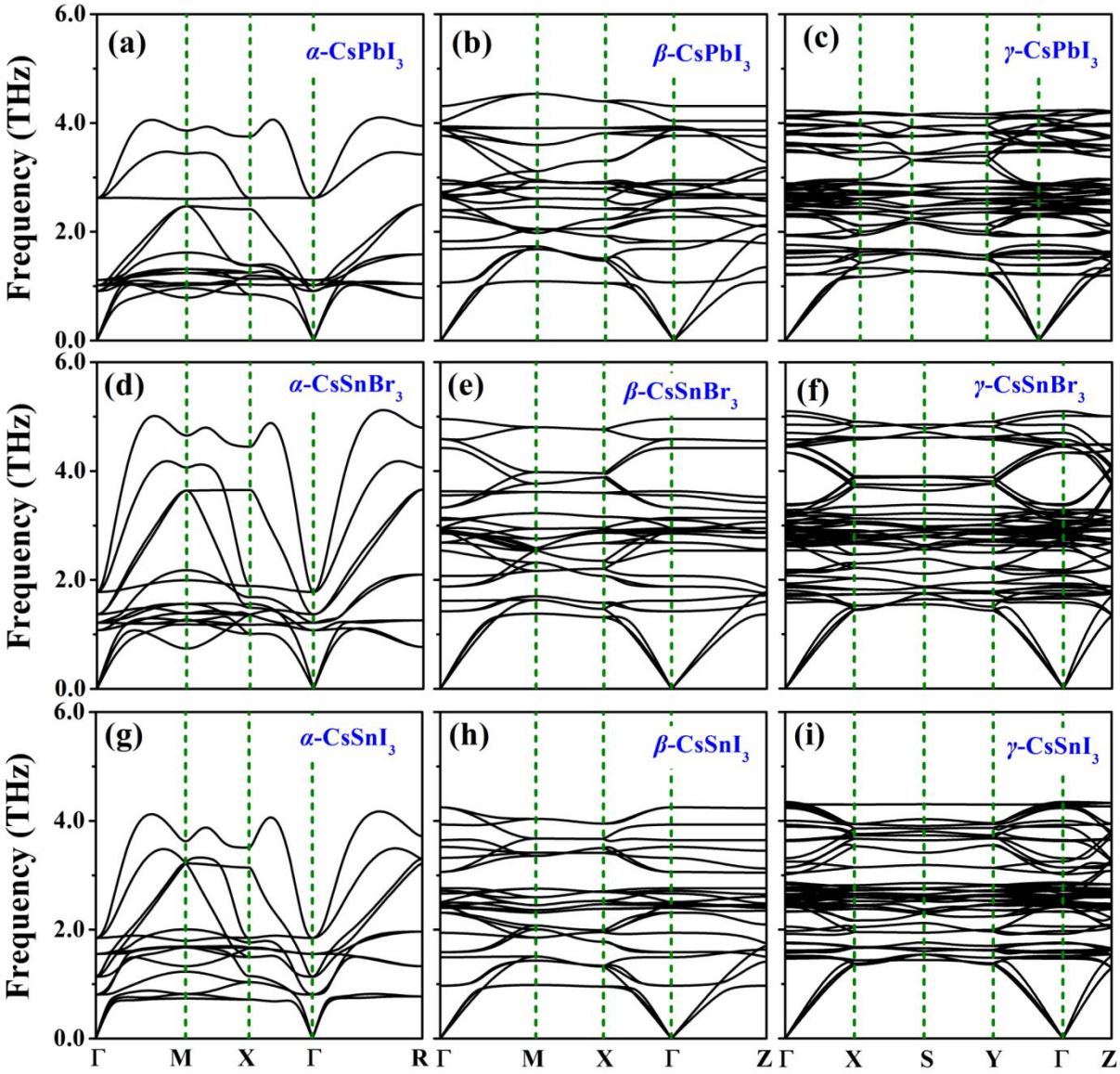

Fig. S1. Phonon spectra of $CsPbI_3$ in (a)-(c), $CsSnBr_3$ in (d)-(f), $CsSnI_3$ in (g)-(i) along the high symmetric directions.

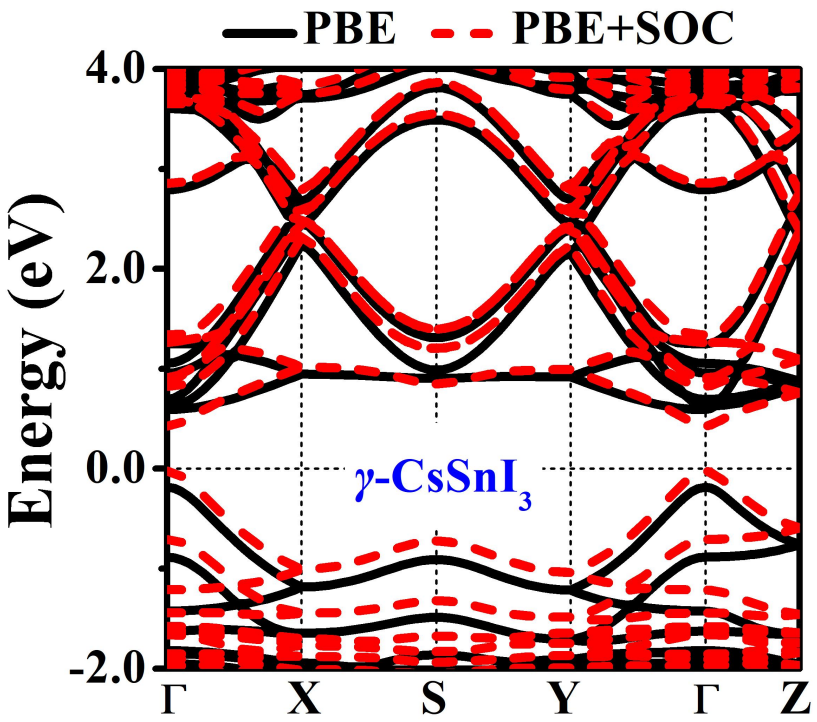

Fig. S2. Band structures of γ-$CsSnI_3$ based on GGA-PBE functional. The dashed lines and solid lines correspond to the band structures with and without considering the SOC effect, respectively.

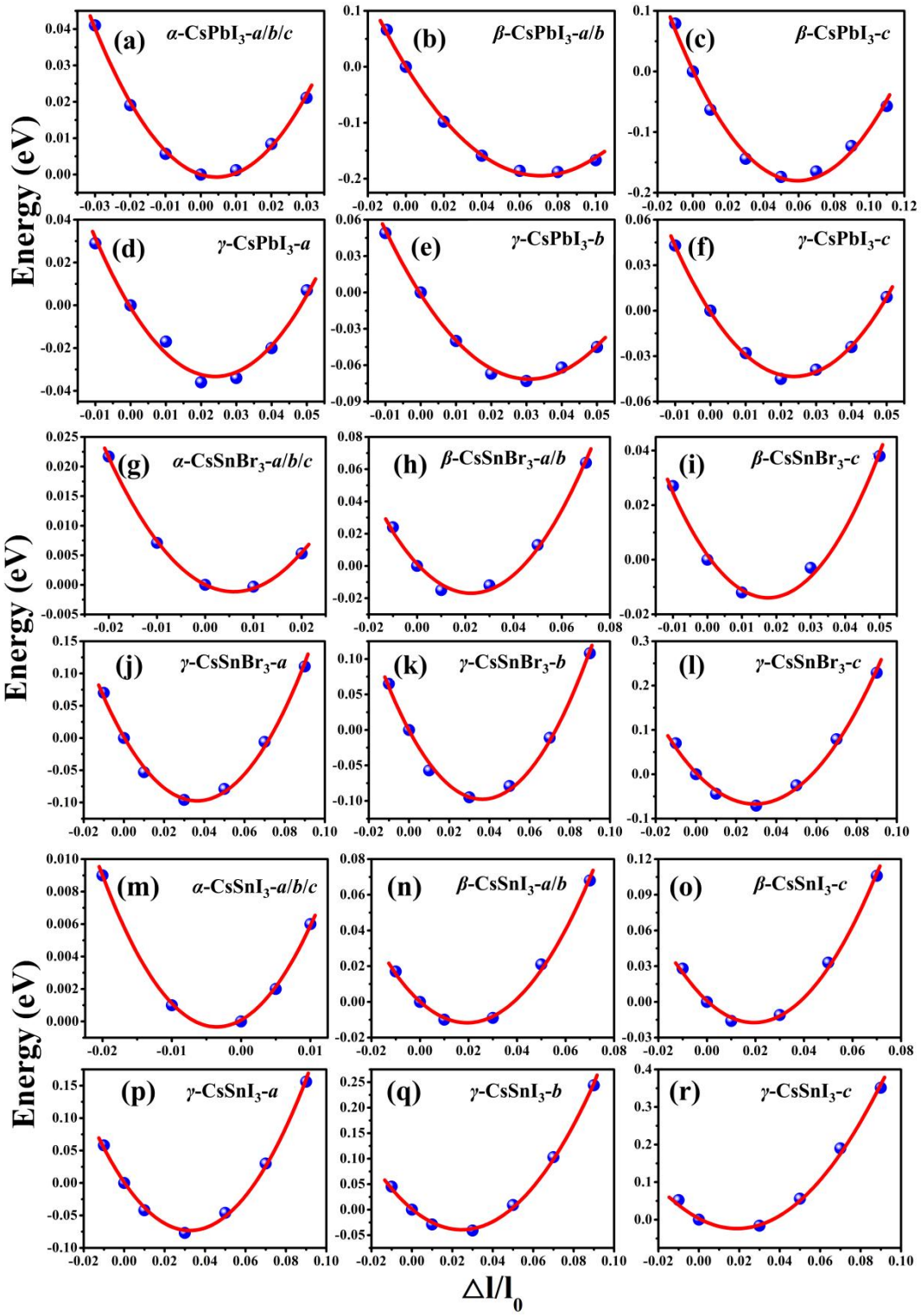

Fig. S3. The total energy difference of $CsPbI_3$ in (a-f), $CsSnBr_3$ in (g-l) and $CsSnI_3$ in (m-r) under different strain relative to the respective pristine system. The blue solid sphere corresponds to the total energy difference of the system under different strain, and the red line represent the quadratic fitting of total energy difference curve.

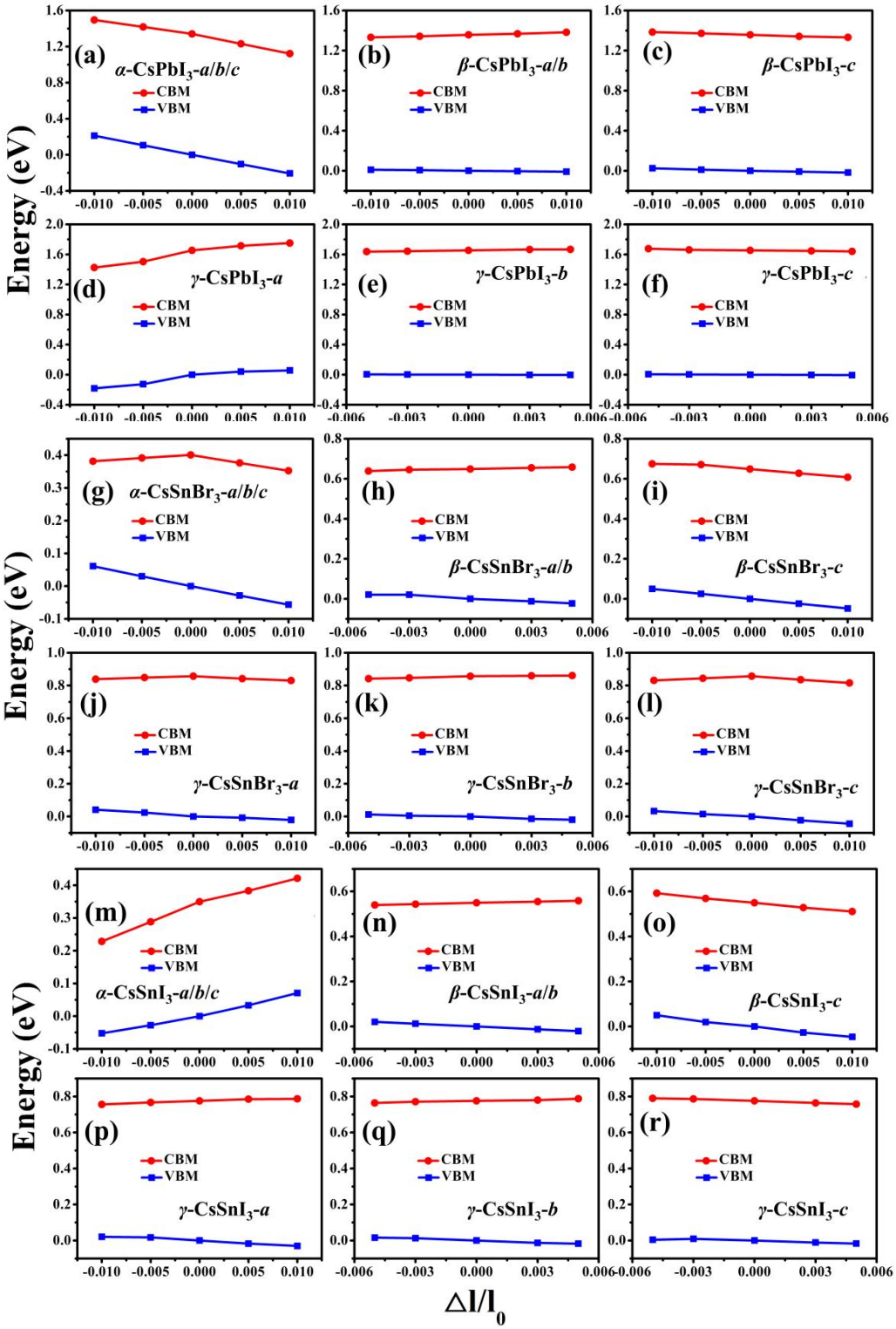

Fig. S4. The CBM and VBM difference of $CsPbI_3$ in (a-f), $CsSnBr_3$ in (g-l) and $CsSnI_3$ in (m-r) under different strain relative to the VBM of the respective pristine system. The deformation potentials can be obtained by linear fitting of the CBMs and VBMs. In particular, for CBMs in (g), (j), (l), the deformation potentials under tensile and compressive stresses are calculated separately, and the average values are taken.

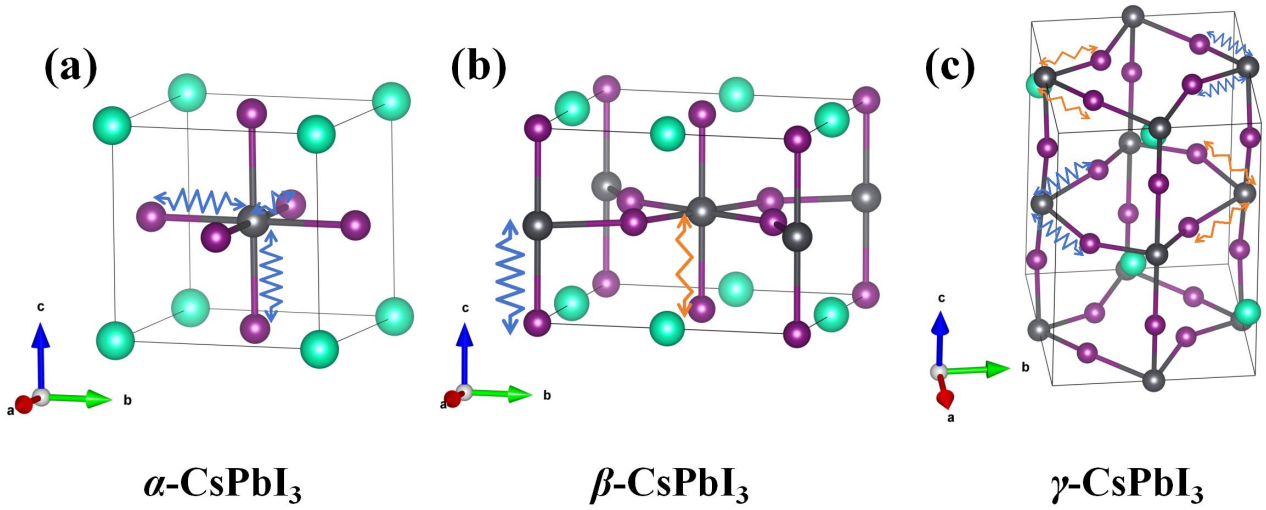

Fig. S5. Optical phonon vibration modes that play major roles in perovskites of α-, β- and γ-$CsPbI_3$. Green balls represent Cs atoms, black balls represent Pb atoms, and purple balls represent I atoms. Blue and orange wavy lines represent opposite vibration directions.

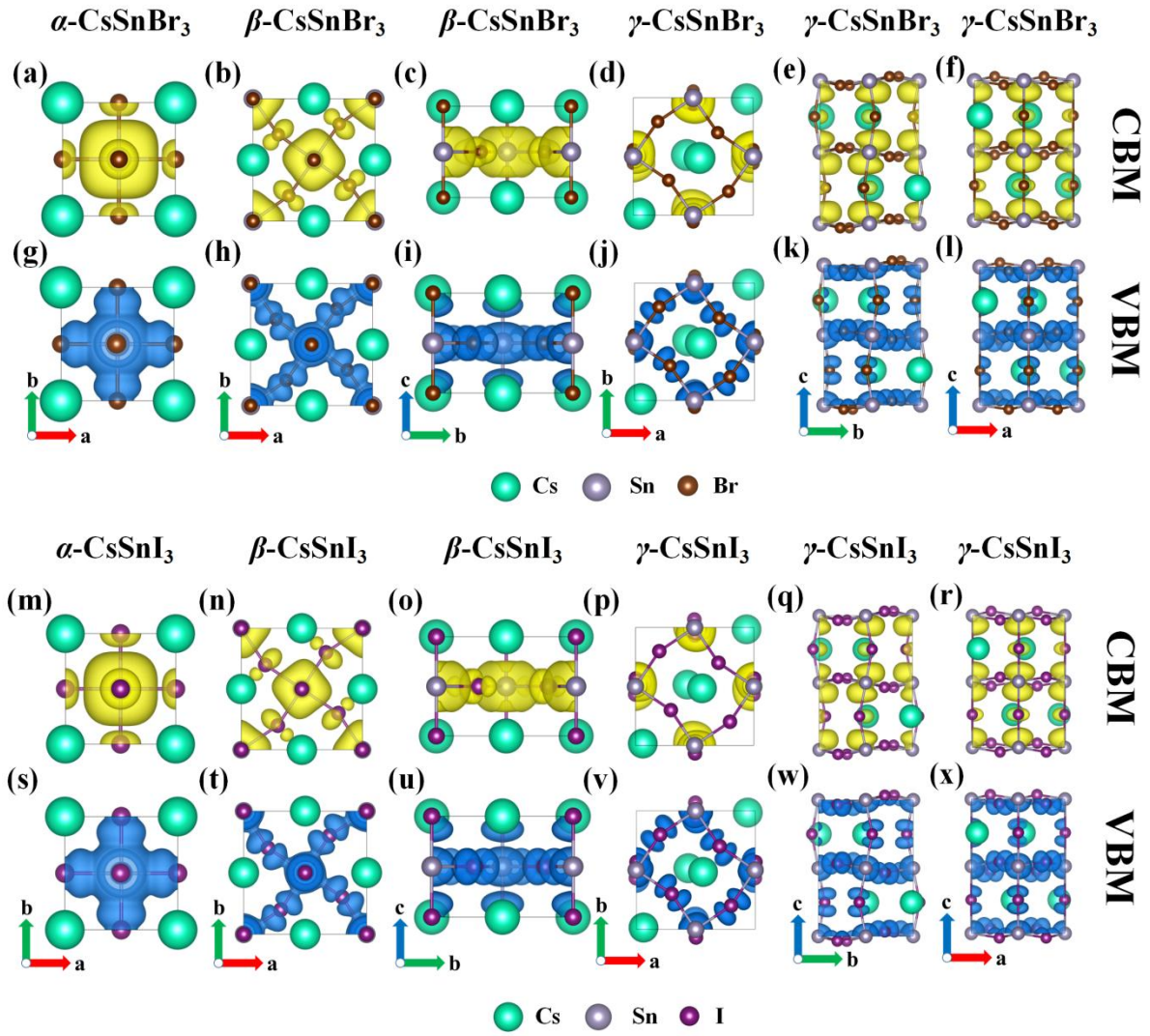

Fig. S6. Partial charge distribution plots of $CsSnBr_3$ in (a)-(l) and $CsSnI_3$ in (m)-(x). The isovalue is 0.01 e/Å^3.

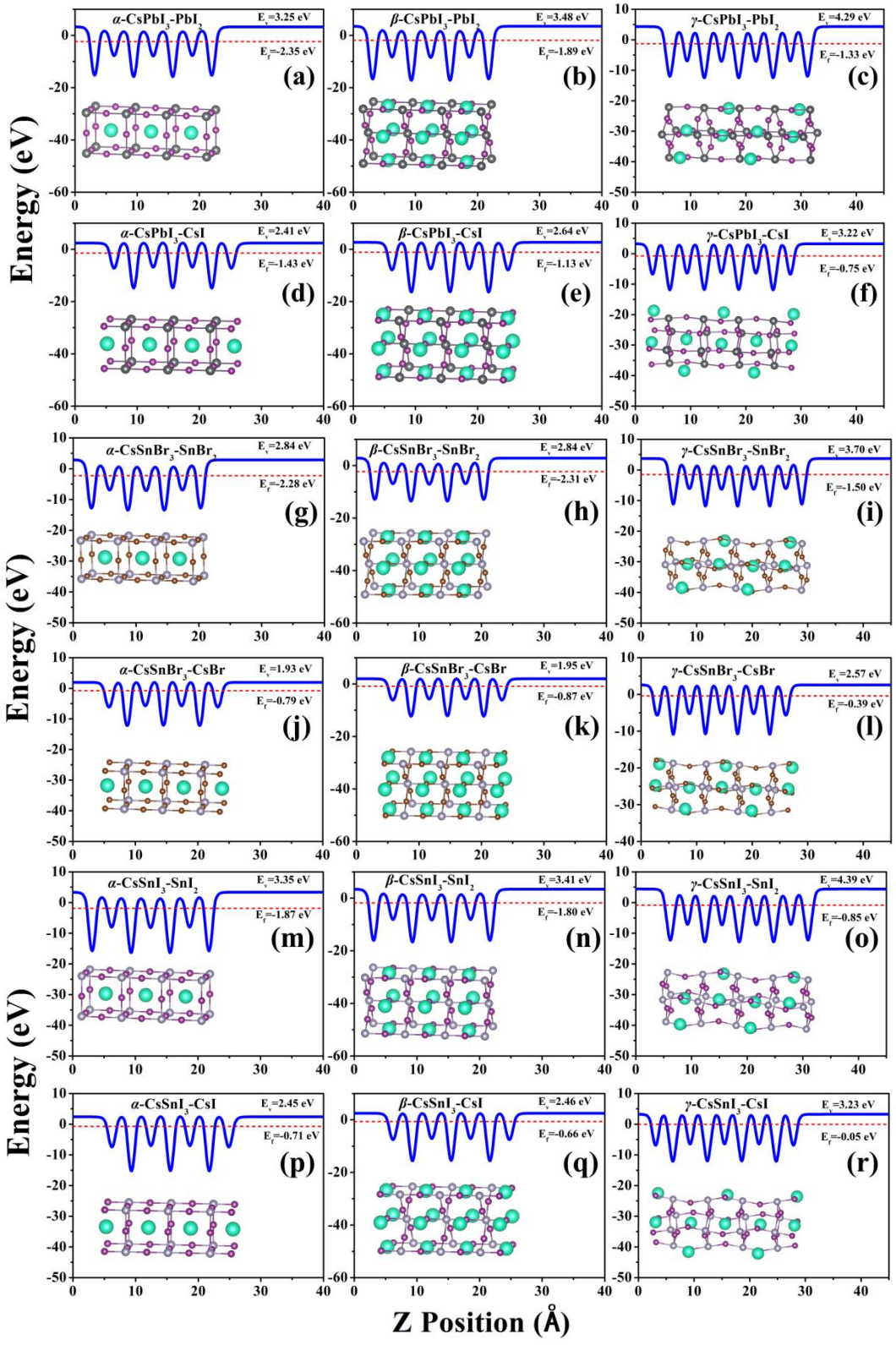

Fig. S7. The *ab* plane-averaged electrostatic potential of $CsPbI_3$-(001) surfaces in (a-f), $CsSnBr_3$-(001) surfaces in (g-l) and $CsSnI_3$-(001) surfaces in (m-r) with BX_2-terminated and CsX-terminated structures. The insets are the corresponding surface models, which corresponds to the electrostatic potential results.

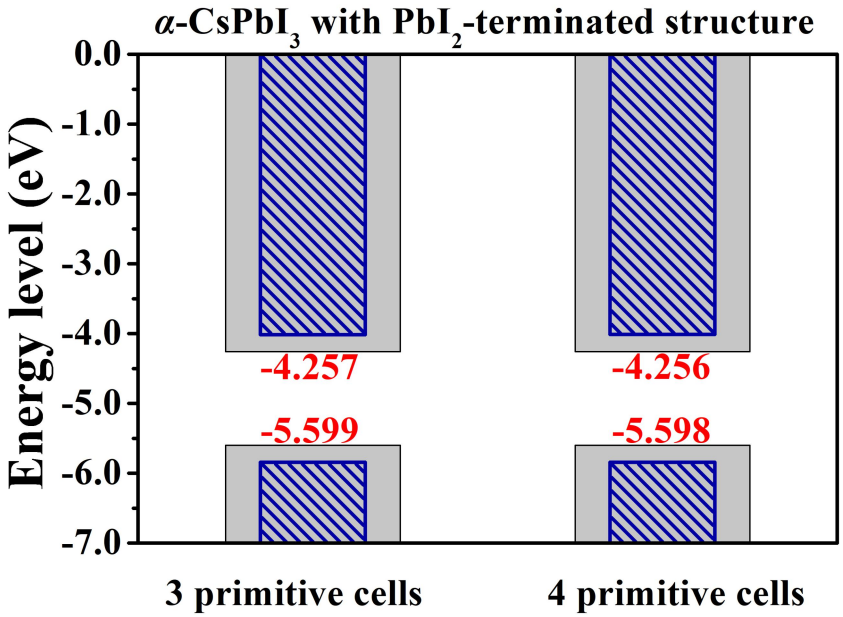

Fig. S8. The band-edge positions of α-$CsPbI_3$ with three primitive cells and four primitive cells.

Table S1. Orbital components of CBM and VBM for $CsBX_3$.

		B-*s*	B-p_x	B-p_y	B-p_z	X-*s*	X-p_x	X-p_y	X-p_z
α-$CsPbI_3$	CBM(R) (%)	/	26.70	26.70	26.70	11.86	/	/	/
	VBM(R) (%)	35.90	/	/	/	/	21.37	21.37	21.37
β-$CsPbI_3$	CBM(Z) (%)	/	/	/	79.65	12.04	/	/	/
	VBM(Z) (%)	34.92	/	/	/	/	21.93	21.93	21.07
γ-$CsPbI_3$	CBM(Γ) (%)	/	10.84	2.21	68.58	10.84	/	/	/
	VBM(Γ) (%)	33.09	/	/	/	/	24.71	19.56	22.65
α-$CsSnBr_3$	CBM(R) (%)	/	27.32	27.32	27.32	10.42	/	/	/
	VBM(R) (%)	43.61	/	/	/	/	18.80	18.80	18.80
β-$CsSnBr_3$	CBM(Z) (%)	/	/	/	82.80	10.40	/	/	/
	VBM(Z) (%)	42.14	/	/	/	/	18.88	18.88	19.98
γ-$CsSnBr_3$	CBM(Γ) (%)	/	0.79	5.56	75.20	9.52	/	/	/
	VBM(Γ) (%)	41.10	/	/	/	/	19.51	19.26	19.75
α-$CsSnI_3$	CBM(R) (%)	/	27.27	27.27	27.27	10.84	/	/	/
	VBM(R) (%)	43.99	/	/	/	/	18.72	18.72	18.72
β-$CsSnI_3$	CBM(Z) (%)	/	/	/	81.82	10.91	/	/	/
	VBM(Z) (%)	42.37	/	/	/	/	18.29	18.29	20.91
γ-$CsSnI_3$	CBM(Γ) (%)	/	0.81	7.33	71.28	9.78	/	/	/
	VBM(Γ) (%)	40.97	/	/	/	/	18.75	20.42	19.72

Table S2. CBM (E_C) and VBM (E_V) of $CsBX_3$-(001) surfaces with BX_2-terminated and CsX-terminated structures based on GGA-PBE and HSE functionals.

	BX_2-terminated				CsX-terminated			
	GGA-PBE		HSE		GGA-PBE		HSE	
	E_V (eV)	E_C (eV)	E_V (eV)	E_C (eV)	E_V (eV)	E_C (eV)	E_V (eV)	E_C (eV)
α-$CsPbI_3$	-5.60	-4.26	-5.85	-4.02	-3.84	-2.50	-4.09	-2.26
β-$CsPbI_3$	-5.37	-4.01	-5.61	-3.77	-3.77	-2.41	-4.01	-2.17
γ-$CsPbI_3$	-5.62	-3.97	-5.89	-3.70	-3.95	-2.30	-4.22	-2.03
α-$CsSnBr_3$	-5.12	-4.72	-5.34	-4.51	-2.72	-2.32	-2.94	-2.11
β-$CsSnBr_3$	-5.15	-4.50	-5.37	-4.29	-2.82	-2.17	-3.04	-1.96
γ-$CsSnBr_3$	-5.20	-4.34	-5.44	-4.11	-2.96	-2.10	-3.20	-1.87
α-$CsSnI_3$	-5.22	-4.87	-5.39	-4.70	-3.16	-2.81	-3.33	-2.64
β-$CsSnI_3$	-5.21	-4.66	-5.38	-4.50	-3.12	-2.57	-3.29	-2.41
γ-$CsSnI_3$	-5.24	-4.46	-5.44	-4.27	-3.28	-2.50	-3.48	-2.31