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Electronic supplementary information for

First-principles study of the surface energies and electronic structures of γ-$CsSnI_3$ surfaces

Tong Zhou [1], Yan-Jin Chen,[1] Chunju Hou[2], 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

Calculating the surface energies of polar surfaces

Sn-rich condition is good for suppressing the formation of Sn-vacancy in $CsSnI_3$, which is considered as the most detrimental defect, promoting high luminescent efficiency.[1] For Sn-perovskites, Sn-rich condition may be achieved by the presence of excess Sn sources such as Sn metal and SnF_2 additive.[2, 3] Nakamura et al. found that Sn metal nanoparticles are produced from the reaction of a dihydropyrizine derivative with SnF_2 (II) additive.[3] Assuming Sn-rich condition (i.e., $\Delta\mu_{Sn}$ =0 eV), we obtain $\Delta\mu_{Cs} + 3\Delta\mu_I = -4.720$ eV for $CsSnI_3$. Combining Sn-rich with CsI-rich ($\Delta\mu_{Cs} + \Delta\mu_I = -3.081$ eV) conditions of stable $CsSnI_3$, we obtain: $\Delta\mu_{Cs} = -2.261\,eV$ and $\Delta\mu_I = -0.820\,eV$. Similarly, we obtain: $\Delta\mu_{Cs} = -2.536\,eV$ and $\Delta\mu_I = -0.728\,eV$ at SnI_2-rich condition ($\Delta\mu_{Cs} + \Delta\mu_I$=−3.264 eV). The surface energies (E_{surf}) of (100), (010) and (101) polar surfaces are calculated at these conditions. In particular, the E_{surf} of (101) surface, either for CsI_3- or Sn-termination, only depends on $\Delta\mu_{Cs} + 3\Delta\mu_I$:

$$E_{surf}^{CsI3} = \lambda_{CsI3} - \frac{1}{S}(\Delta\mu_{Cs} + 3\Delta\mu_I) \quad (1)$$

$$E_{surf}^{Sn} = \lambda_{Sn} + \frac{1}{S}(\Delta\mu_{Cs} + 3\Delta\mu_I) \quad (2)$$

For Sn-rich condition, the E_{surf} of (101) surfaces can be calculated according to $\Delta\mu_{Cs} + 3\Delta\mu_I = -4.720$ eV and thus is independent of CsI-rich or SnI_2-rich condition.

Effect of dispersion force on the structures and surface energies

To show the effect of London dispersion force on the structures and surface energies, we use PBEsol+D3[4] to calculate the structural parameters of $CsSnI_3$ bulk and the surface energies of (001) surfaces. It is seen from Table S2 that the structural parameters calculated by PBEsol and PBEsol+D3 are consistent with each other and agree well with experimental values. From Table S3, one can find that the surface energies of the CsI-(001) and SnI_2-(001) surfaces calculated from PBEsol+D3 are overall increased by 0.07 and 0.11 J/m^2, respectively, in comparison with the values obtained from PBEsol. It is worth noting that the difference in the surface energies between SnI_2-(001) and CsI-(001) surfaces increase about 0.04 J/m^2, indicating that CsI-termination remains the most stable compared with SnI_2-termination with the consideration of London dispersion force. Therefore, including London dispersion force in the calculations does not change the main conclusions based on PBEsol.

Table S1 Surface energies (E_{surf}, J/m^2) of the $CsSnI_3$ (001) surfaces calculated by using the cutoff values of 350 eV and 500 eV.

E_{surf}	350 eV		500 eV	
Terminations	CsI-rich	SnI_2-rich	CsI-rich	SnI_2-rich
CsI-(001)	0.073	0.113	0.071	0.110
SnI_2-(001)	0.196	0.156	0.194	0.154

Table S2 Structural parameters of γ-$CsSnI_3$ calculated by using PBEsol and PBEsol+D3. Experimental (Expt.) values[5] are also listed here for a comparison.

	a（Å）	b	c
PBEsol	8.779	8.344	12.238
PBEsol+D3	8.525	8.510	12.225
Expt.	8.688	8.643	12.378

Table S3 Surface energies (E_{surf}, J/m^2) of γ-$CsSnI_3$ (001) surfaces calculated by using PBEsol and PBEsol+D3.

E_{surf}	PBEsol		PBEsol+D3	
Terminations	CsI-rich	SnI_2-rich	CsI-rich	SnI_2-rich
CsI-(001)	0.073	0.113	0.141	0.185
SnI_2-(001)	0.196	0.156	0.309	0.265

Table S4 Surface energies (E_{surf}, J/m^2) of the (100), (010) and (101) polar surfaces. Assuming Sn-rich condition (i.e., $\Delta\mu_{Sn}$ =0 eV), the E_{surf} are calculated at CsI-rich: $\Delta\mu_{Cs} = -2.261\,eV$ and $\Delta\mu_I = -0.820\,eV$, and SnI_2-rich condition: $\Delta\mu_{Cs} = -2.536\,eV$ and $\Delta\mu_I = -0.728\,eV$.

E_{surf}	(100)		(010)		(101)	
	CsSnI	I_2	CsSnI	I_2	CsI_3	Sn
CsI-rich	0.467	0.312	0.449	0.312	0.243	0.418
SnI_2-rich	0.496	0.283	0.477	0.285	0.243	0.418

Table S5 E_{surf} (J/m^2) of polarity-compensated (010) surface. Three terminations (Cs, SnI and I) are considered for (010) surface. The E_{surf} values are calculated at the CsI-rich ($\Delta\mu_{Cs}+\Delta\mu_I$=-3.081 eV) and SnI_2-rich ($\Delta\mu_{Cs}+\Delta\mu_I$=-3.264 eV) conditions.

E_{surf}	(010)		
	Cs	SnI	I
CsI-rich	0.120	0.231	0.118
SnI_2-rich	0.175	0.177	0.118

Table S6 E_{surf} (J/m^2) of the (100) and (001) surfaces of $CsSnI_3$ and $CsPbI_3$. The E_{surf} of the (100) and (001) surfaces of $CsPbI_3$ are taken from a previous study.[6]

		(100)					(001)	
M	E_{surf}	Cs	MI	CsMI	I_2	I	CsI	MI_2
Sn	CsI-rich	0.119	0.246	0.467	0.312	0.118	0.073	0.196
	SnI_2-rich	0.176	0.189	0.496	0.283	0.118	0.113	0.156
Pb	CsI-rich	0.112	0.252	0.465	0.532	0.130	0.069	0.193
	PbI_2-rich	0.137	0.228	0.477	0.520	0.130	0.085	0.177

Table S7 Band gaps (E_g) of the (110), (001), (100) and (101) surfaces of $CsSnI_3$. The calculated band gap of the bulk is 0.53 eV. Nine-layers slabs are used for the (110) and (001) surfaces; thirteen-layers slabs for the (100)-Cs, (100)-SnI and (100)-I surfaces; fifteen-layers for the (101)-CsI_2 and (101)-I^*. These choices ensure a similar thickness of about 29 Å for all these slabs. Orbital-projected band structures and the effective masses in the main text and ESI are calculated using these slabs.

Surfaces	(110)		(001)		(100)			(101)	
Terminations	CsI	SnI_2	CsI	SnI_2	Cs	SnI	I	CsI_2	I^*
E_g	0.68	0.65	0.72	0.64	0.87	0.80	0.83	0.88	0.99

Table S8 Calculated effective mass (in units of the free-electron mass m_0) of hole (m_h) and electron (m_e) along Γ-M for the (110), (001), (100) and (101) surfaces.

Surfaces	(110)		(001)		(100)			(101)	
Terminations	CsI	SnI_2	CsI	SnI_2	Cs	SnI	I	CsI_2	I*
m_h	0.26	0.26	0.31	0.34	0.54	0.39	0.45	0.65	0.73
m_e	0.30	0.74	0.36	0.41	0.55	0.97	0.52	1.06	2.41

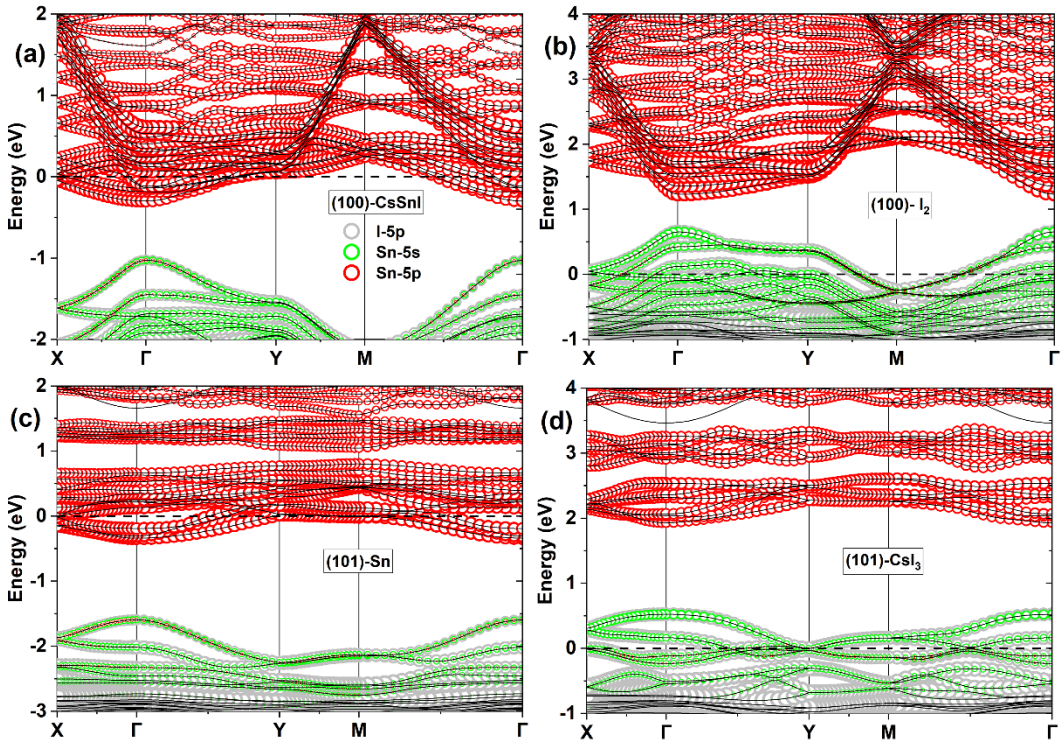

Figure S1 Orbital-projected band structures of the CsSnI- and I_2-terminated (100) surfaces, and the Sn- and CsI_3-terminated (101) surfaces. The Fermi level is indicated by the horizontal dashed line.

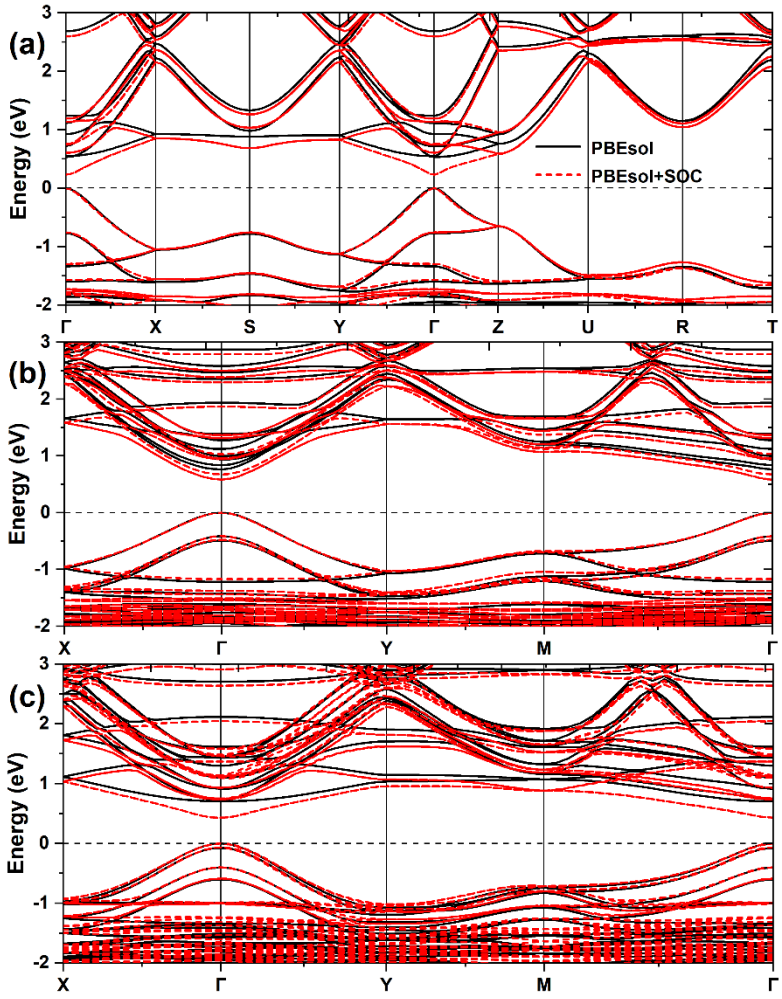

Figure S2 Band structures calculated without (PBEsol) and with SOC (PBEsol+SOC) for: (a) the bulk; (b) CsI-(001) surface; (c) SnI_2-(001) surface. The energy of the VBM is set as zero. Seven-layers slabs are used for the (001) surfaces.

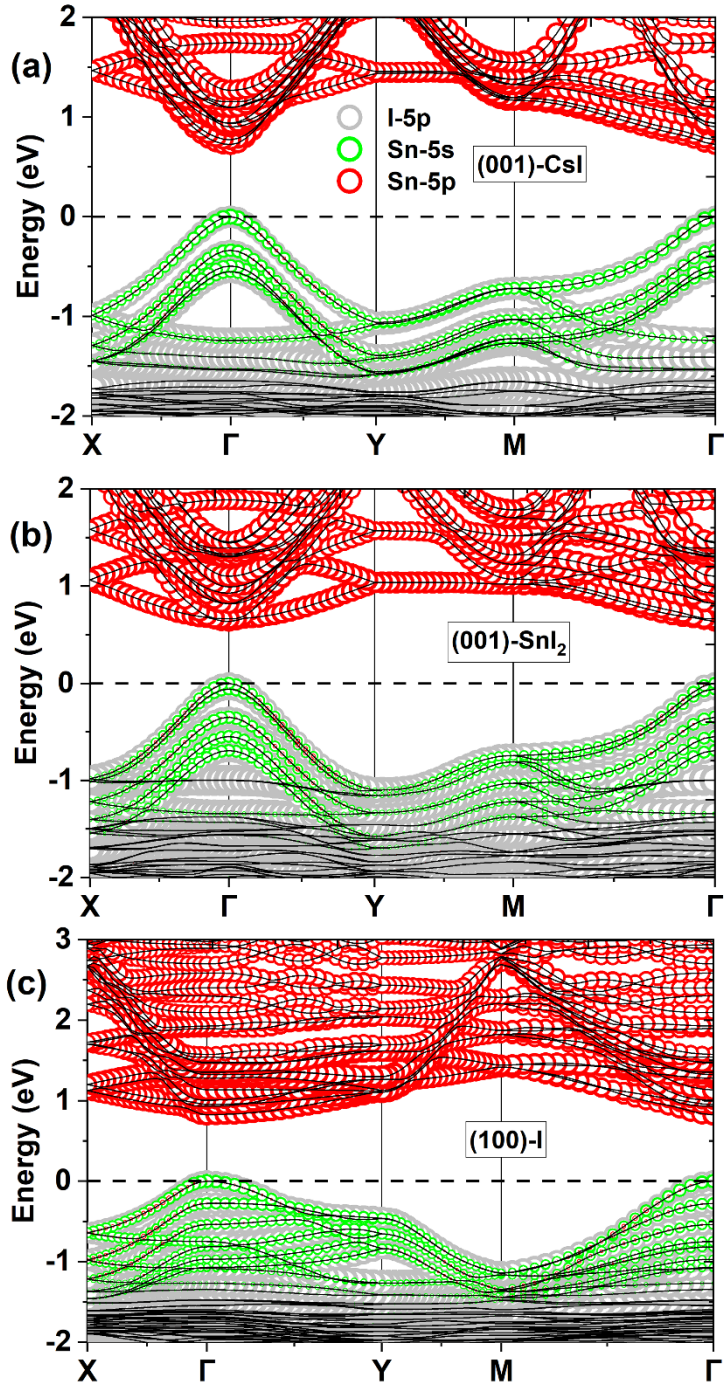

Figure S3 Orbital-projected band structures of the (001)-CsI, (001)-SnI_2 and (100)-I surfaces. The energy of the VBM is set as zero.

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