

Supporting Information

Alloy Engineering in Mixed Sn-Ge Perovskites for Photovoltaic Application

Yu-Qian Zhou,[†] Jian Xu,[†] Jian-Bo Liu,^{*,†} and Bai-Xin Liu[†]

[†]*Key Laboratory of Advanced Materials (MOE), School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China*

**Corresponding Author:*

Jian-bo Liu (E-mail: jbliu@mail.tsinghua.edu.cn)

Note 1: Computational details of effective carrier masses

Effective carrier masses m can be evaluated as

$$m = \hbar \left[\frac{\partial^2 E(k)}{\partial^2 k} \right]^{-1}$$

where $E(k)$ are the energy dispersion relation functions described by band structures, and \hbar is the reduced Planck constant.

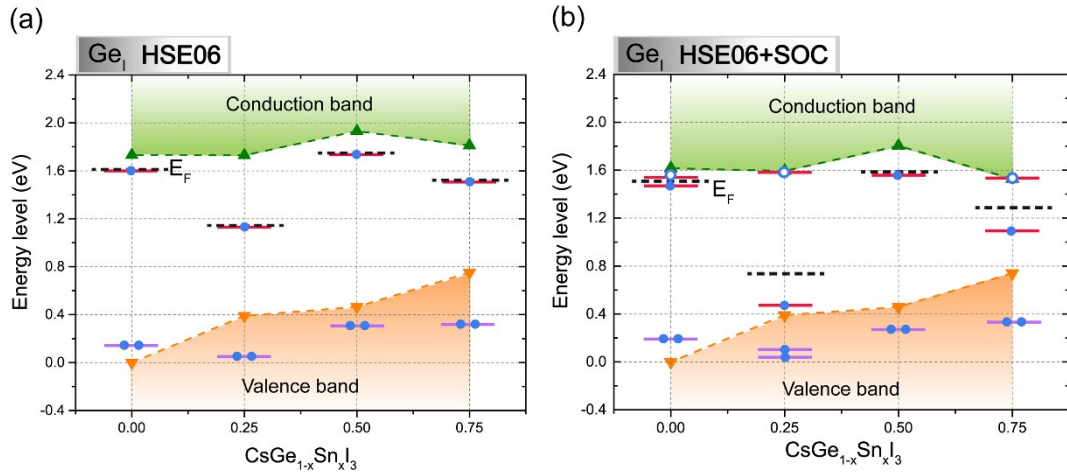


Figure S1. Schematic diagrams of the defect levels of Ge_I in $\text{CsGe}_{1-x}\text{Sn}_x\text{I}_3$ ($x = 0, 0.25, 0.50, 0.75$) by (a) the HSE06 method without SOC and (b) the HSE06 + SOC method. The 1s core level of Cs is used for alignment and the VBM of CsGeI_3 is set to 0. The solid circles in blue represent electrons, while the hollow circles indicate holes. The Fermi level (E_F) is shown as a black dotted line.

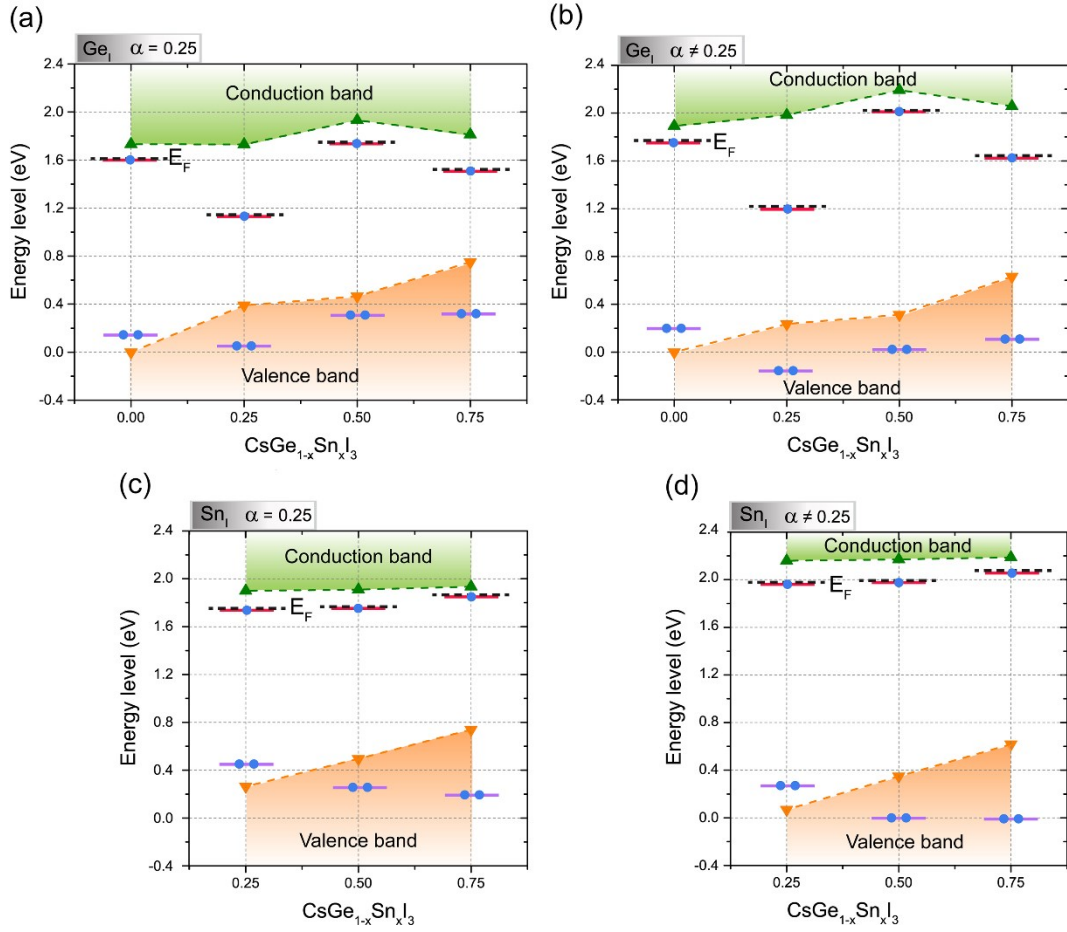


Figure S2. Schematic diagrams of the defect levels of Ge_I and Sn_I in $\text{CsGe}_{1-x}\text{Sn}_x\text{I}_3$ ($x = 0.25, 0.50, 0.75$) by the HSE method with different mixing parameter (α): (a) Ge_I with $\alpha = 0.25$ (HSE06), (b) Ge_I with $\alpha \neq 0.25$, (c) Sn_I with $\alpha = 0.25$ (HSE06), and (d) Sn_I with $\alpha \neq 0.25$. CsGeI_3 is also shown for comparison. For HSE with $\alpha \neq 0.25$, the α of CsGeI_3 is set to 0.32 to fit the experimental bandgap of 1.6 eV¹, and the α of $\text{CsGe}_{0.5}\text{Sn}_{0.5}\text{I}_3$ ($x = 0.50$) is set to 0.45 to fit the experimental bandgap of 1.5 eV². For $\text{CsGe}_{0.75}\text{Sn}_{0.25}\text{I}_3$ ($x = 0.25$) and $\text{CsGe}_{0.25}\text{Sn}_{0.75}\text{I}_3$ ($x = 0.75$), the same α as $\text{CsGe}_{0.5}\text{Sn}_{0.5}\text{I}_3$ ($x = 0.50$) are used, since the experimental bandgap of them is not available yet. The 1s core level of Cs is used for alignment and the VBM of CsGeI_3 is set to 0. The solid circles in blue represent electrons and the Fermi level is shown as a black dotted line.

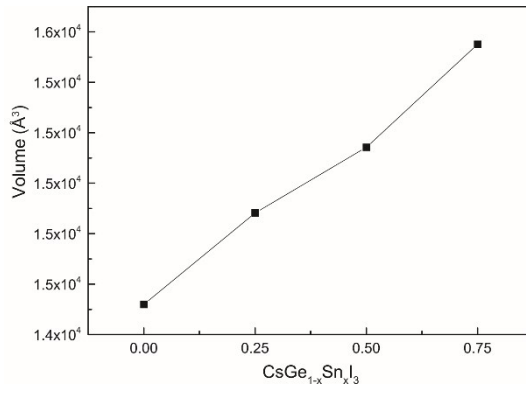


Figure S3. Volume change with Sn concentration (x) for $\text{CsGe}_{1-x}\text{Sn}_x\text{I}_3$ ($x = 0, 0.25, 0.5, \text{ and } 0.75$).

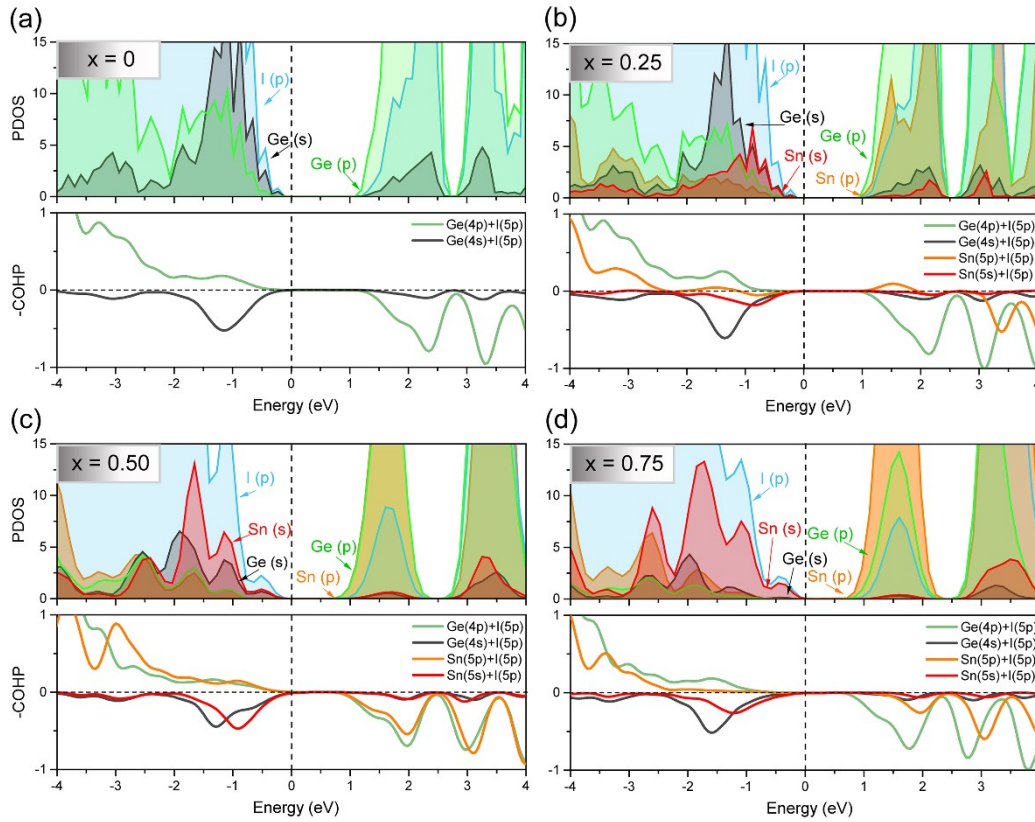


Figure S4. Orbital-projected density of states (DOS) and projected crystal orbital hamilton population (COHP) for $\text{CsGe}_{1-x}\text{Sn}_x\text{I}_3$: (a) $x = 0$ (CsGeI_3), (b) $x = 0.25$ ($\text{CsGe}_{0.75}\text{Sn}_{0.25}\text{I}_3$), (c) $x = 0.50$ ($\text{CsGe}_{0.5}\text{Sn}_{0.5}\text{I}_3$), and (d) $x = 0.75$ ($\text{CsGe}_{0.25}\text{Sn}_{0.75}\text{I}_3$). The Fermi level is set to zero.

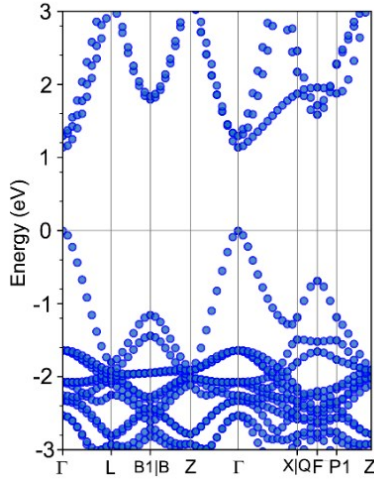


Figure S5. Unfolded band structure for $\text{CsGe}_{0.5}\text{Sn}_{0.5}\text{I}_3$.

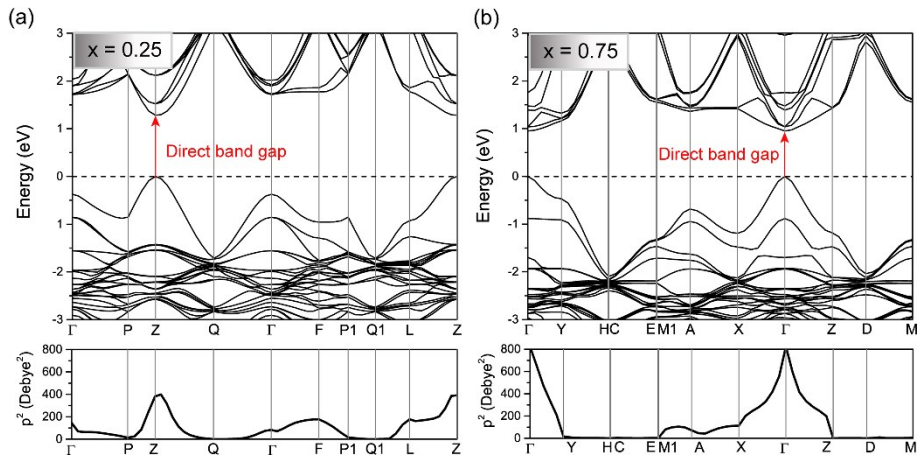


Figure S6. HSE06 calculated band structure (top panel) and optical transition dipole moment (bottom panel) for (a) $\text{CsGe}_{0.75}\text{Sn}_{0.25}\text{I}_3$ ($x = 0.25$) and (b) $\text{CsGe}_{0.25}\text{Sn}_{0.75}\text{I}_3$ ($x = 0.75$).

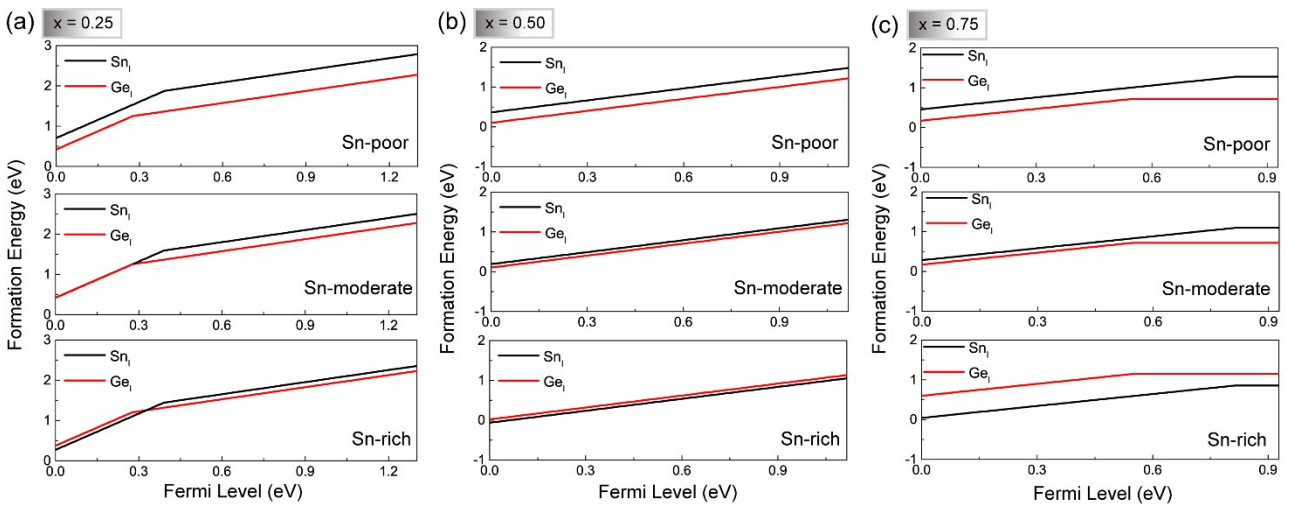


Figure S7. Calculated formation energies of Ge_I and Sn_I defects with different charge states q in $\text{CsGe}_{1-x}\text{Sn}_x\text{I}_3$ as a function of the Fermi level: (a) $x = 0.25$, (b) $x = 0.5$, and (c) $x = 0.75$. The slope of the line segments indicates the defect charge states, and the kinks denote the transition energy levels. The Fermi

level is referenced to the host VBM.

Note 2: Computational details of defect formation energies

The formation energy $E^f[X^q]$ of defect X in charge state q as a function of the Fermi level E_F can be evaluated as³

$$E^f[X^q] = E_{\text{tot}}[X^q] - E_{\text{tot}}[P] + \sum_i n_i \mu_i + q(\varepsilon_{\text{VBM}} + E_F) + E_{\text{align}}[X^q] \quad (1)$$

where $E_{\text{tot}}[X^q]$ and $E_{\text{tot}}[P]$ are the total energy for defective supercells and the corresponding perfect crystal, respectively. The number of atoms of type i that have been added to ($n_i < 0$) or removed from ($n_i > 0$) the supercell is indicated by n_i . μ_i is the corresponding chemical potential. ε_{VBM} is the eigenvalue of valence-band maximum (VBM) in the perfect crystal and E_F is the Fermi level that refers to the VBM. $E_{\text{align}}[X^q]$ (i.e., $q\Delta V$) is a correction term for potential-alignment to correct the finite-size effects in charged systems.^{4, 5} The CTLs $\varepsilon(q_1/q_2)$ are defined as the Fermi-level positions at which the formation energy of charge states q_1 is equal to that of q_2 :^{6, 7}

$$\varepsilon(q_1/q_2) = \frac{(E_{\text{tot}}[X^{q_1}] + E_{\text{align}}[X^{q_1}]) - (E_{\text{tot}}[X^{q_2}] + E_{\text{align}}[X^{q_2}])}{(q_2 - q_1)} - \varepsilon_{\text{VBM}} \quad (2)$$

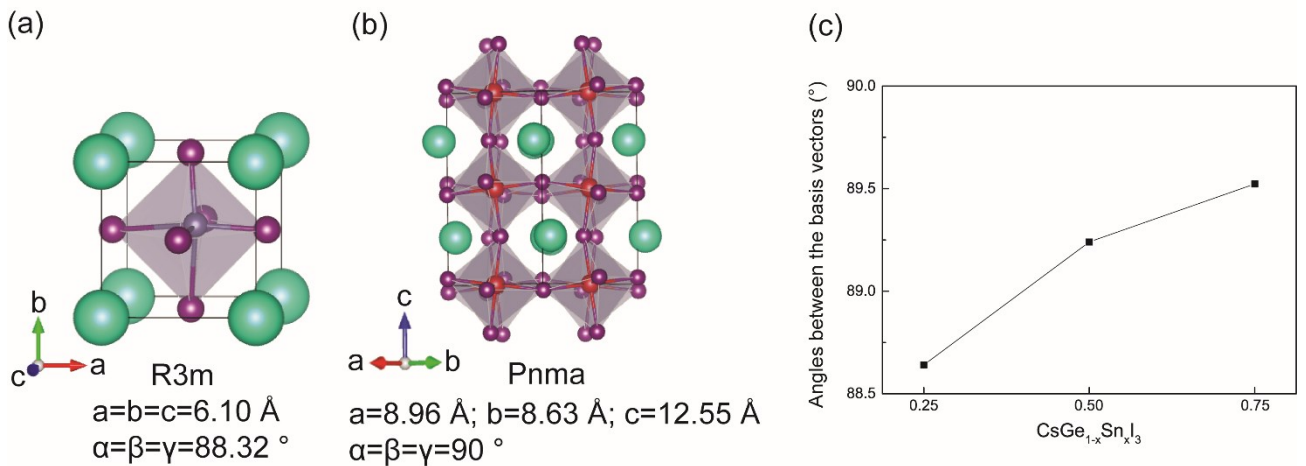


Figure S8. Crystal structures of (a) CsGeI_3 and (b) CsSnI_3 . Green, gray, red, and purple balls indicate Cs, Ge, Sn, and I atoms, respectively. (c) The angles between the basis vectors of $\text{CsGe}_{1-x}\text{Sn}_x\text{I}_3$ alloys. For $x = 0.75$, the average bond angle is shown.

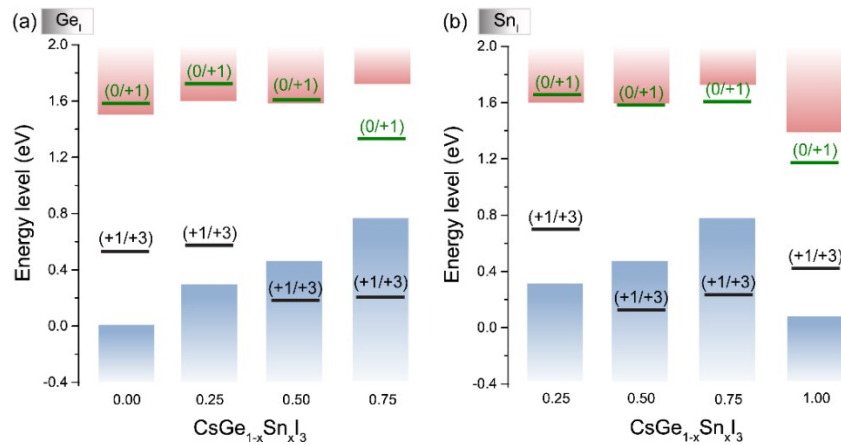


Figure S9. Calculated transition energy levels for (a) Ge_I and (b) Sn_I in $\text{CsGe}_{1-x}\text{Sn}_x\text{I}_3$ ($x = 0.25, 0.50,$ and 0.75). CsGeI_3 and CsSnI_3 (space group Pnma) are also shown for comparison. The $1s$ core level of Cs is used for alignment and the VBM of CsGeI_3 is set to 0.

References:

1. C. C. Stoumpos, L. Frazer, D. J. Clark, Y. S. Kim, S. H. Rhim, A. J. Freeman, J. B. Ketterson, J. I. Jang and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2015, **137**, 6804-6819.
2. M. Chen, M.-G. Ju, H. F. Garces, A. D. Carl, L. K. Ono, Z. Hawash, Y. Zhang, T. Shen, Y. Qi, R. L. Grimm, D. Pacifici, X. C. Zeng, Y. Zhou and N. P. Padture, *Nat. Commun.*, 2019, **10**, 16.
3. C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti and C. G. Van de Walle, *Rev. Mod. Phys.*, 2014, **86**, 253-305.
4. T. Mattila and A. Zunger, *Phys. Rev. B*, 1998, **58**, 1367-1373.
5. S. Lany and A. Zunger, *Modell. Simul. Mater. Sci. Eng.*, 2009, **17**, 084002.
6. G. Y. Yonggang, X. Zhang and A. Zunger, *Phys. Rev. B*, 2017, **95**, 085201.
7. C. Freysoldt, B. Lange, J. Neugebauer, Q. Yan, J. L. Lyons, A. Janotti and C. G. Van de Walle, *Phys. Rev. B*, 2016, **93**, 165206.