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Intrinsic defects in photovoltaic perovskite variant Cs_2SnI_6

Zewen Xiao,*[ab] Yuanyuan Zhou,[c] Hideo Hosono,[ab] and Toshio Kamiya*[ab]

Supplementary Information:

Computational details. Ground-state structures, electronic structures, and defect formation energies were calculated in the framework of DFT and hybrid DFT using the projector-augmented wave (PAW) method as implemented in the VASP code.[S1] Cs (5s)(5p)(6s), Sn (5s)(5p), and I (5s)(5p) orbitals are treated as valence states in the PAW potentials. The cutoff energy for the basis set was set to 275.4 eV.

First we checked k-point convergence for the primitive cell of the ideal Cs_2SnI_6 crystal and confirmed 3x3x3 or denser k-meshes provided well-converged results with energy differences less than 10 meV / atom; therefore, we employed 4x4x4 k-mesh for the calculation of the ideal model.

A 72-atoms supercell (2×2×2 primitive cells) was used to model the intrinsic defects. Atomic positions were relaxed until all the forces on the atoms were less than 0.05 eV/Å, employing a Γ-centered 3×3×3 *k*-mesh (corresponds to 6×6×6 k-mesh for the primitive cell) and the Perdew−Burke−Ernzerhof (PBE96)[S2] generalized gradient approximation (GGA) functionals. The total energies were calculated using the Heyd−Scuseria−Ernzerhof (HSE06)[S3,S4] hybrid functional with 34% of exact nonlocal exact exchange, which was adjusted to reproduce the experimental band gap of 1.26 eV.[S5] Here, we employed the Γ point only calculation for two reasons. One is that we should avoid to include interference between the defects in neighboring supercells. The other reason is that we employed the HSE06 hybrid DFT calculations take a long time, which limited the k-mesh only to the Γ point. We assessed the possible error caused by the Γ point only calculations for representative defects; e.g., the calculated the formation enthalpies of defects (ΔH) of the Γ point only calculations & the 2×2×2 *k*-mesh calculations were 0.84 & 0.74 eV for V_I, 1.69 & 1.61 eV for V_{Cs}, and 2.76 & 2.77 eV for Sn_I at the A potential point. These errors are within 0.1 eV and do not affect the conclusions of the present study.

ΔH of a defect (D) in a charge state q was calculated through the following equation[S6]

$$\Delta H_{D,q}(E_F,\mu) = E_{D,q} - E_H - \Sigma n_\alpha \mu_\alpha + q(E_F+E_V), \quad (S1)$$

where $E_{D,q}$ is the total energies of the supercell with the defect D in the charge state q, and E_H that of the perfect host supercell. n_α indicates the number of α atoms added ($n_\alpha > 0$) or removed ($n_\alpha < 0$), and μ_α is the chemical potential of an α atom with respect to that of an elemental phase (μ_α^{el}) by $\mu_\alpha = \mu_\alpha^{el} + \Delta\mu_\alpha$. E_F is the Fermi level relative to the valence band maximum (VBM, E_V).

For charged defects, the total number of valence electrons were varied as implemented in the VASP code. The potential alignment correction and the image charge correction were applied to correct the supercell finite-size effects.[S6,S7] For the potential alignment correction, the average electrostatic potential at the atomic sites far from the defects was aligned with that in the ideal crystal, and the resulting difference ΔV was added to the E_V in Eq. S1. The image charge correction (ΔE_i) was calculated using the simplified expression[S7]

$$\Delta E_i = ⅔\, \Delta E_i^1 = ⅔\, (q^2\alpha_M/L)/\varepsilon, \quad (S2)$$

where α_M is the Madelung constant, $L = \Omega^{-1/3}$ is the linear supercell dimension (Ω is the supercell volume), and ε is the dielectric constant (the calculated value of 3.88 was used here). The bracketed term in Equation S2 was calculated by the VASP code and printed in the OUTCAR file.

From the $\Delta H_{D,q}$, the defect transition level $\varepsilon(q/q')$ between two charge states q and q' is obtained as the E_F where $\Delta H_{D,q}(E_F,q) = \Delta H_{D,q'}(E_F, q')$. The defect concentrations were calculated by the following equation[S8]

$$c_{D,q}(E_F,\mu,T) = N_{D,q}\exp[\Delta S_{D,q}/k_B - \Delta H_{D,q}(E_F,\mu)/k_B T_D], \quad (S3)$$

where $N_{D,q}$ is the density of the defect sites, $\Delta S_{D,q}$ the formation entropy (typically taken to be $5k_B$[S8]), k_B the Boltzmann constant, and T_D the growth temperature, where we assume that defects formed at T_D were frozen to the room temperature. The equilibrium E_F ($E_{F,e}$) and $c_{D,q}$ at room temperature (i.e. measurement temperature) for given μ and T_D were determined by solving the following semiconductor statistic equations self-consistently so as to satisfy the charge neutrality.[S8]

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[a] Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan
Email: zwxiao7@gmail.com, kamiya.t.aa@m.titech.ac.jp
[b] Materials Research Center for Element Strategy, Tokyo Institute of Technology, Yokohama 226-8503, Japan
[c] School of Engineering, Brown University, Providence, RI 02912, United States

$$\sum_i \sum_j q_i C_{\mathrm{D}_j, q_i} + N_\mathrm{h} - N_\mathrm{e} = 0\,, \tag{S4}$$

$$N_\mathrm{e} = \int_{E_C}^{\infty} D_\mathrm{C}(E) f_\mathrm{e}(E, E_\mathrm{F,e}, T)\, dE\,, \tag{S5}$$

$$N_\mathrm{h} = \int_{-\infty}^{E_V} D_\mathrm{V}(E)\left[1 - f_\mathrm{e}(E, E_\mathrm{F,e}, T)\right] dE\,, \tag{S6}$$

where N_e is the electron density in the conduction band (CB), N_h is the hole density in the valence band (VB), $D_\mathrm{C}(E)$ is the CB density of states, $D_\mathrm{V}(E)$ is the VB density of states, and $f_\mathrm{e}(E, E_\mathrm{F,e}, T)$ is the Fermi-Dirac distribution function with the Fermi energy of $E_\mathrm{F,e}$, and temperature T.

μ_α varies depending on the experimental growth conditions. The chemical potentials of elemental phases $\mu_\mathrm{Cs}{}^\mathrm{el}$, $\mu_\mathrm{Sn}{}^\mathrm{el}$, and $\mu_\mathrm{I}{}^\mathrm{el}$ are taken from elemental Cs (the cubic phase, space group *Fm*–3*m*),[S9] β-Sn (tetragonal, space group *I*4$_1$/*amd*),[S10] and $\mathrm{I_2}$ (orthorhombic, space group *Cmca*),[S11] respectively. First, to stabilize the $\mathrm{Cs_2SnI_6}$ phase, the following thermodynamic equation must be satisfied

$$2\Delta\mu_\mathrm{Cs} + \Delta\mu_\mathrm{Sn} + 6\Delta\mu_\mathrm{I} = \Delta H(\mathrm{Cs_2SnI_6}) = -10.49\ \mathrm{eV}, \tag{S7}$$

where $\Delta H(\mathrm{Cs_2SnI_6})$ is ΔH of $\mathrm{Cs_2SnI_6}$ referred to the elemental Cs, Sn, and I. To avoid the coexistence of the Cs, the Sn, and the $\mathrm{I_2}$ elemental phases, the additional conditions, $\Delta\mu_\mathrm{Cs} < 0$, $\Delta\mu_\mathrm{Sn} < 0$, and $\Delta\mu_\mathrm{I} < 0$, are required. To exclude the secondary phases CsI (cubic, space group *Pm*−3*m*),[S12] $\mathrm{SnI_2}$ (monoclinic, space group *C*2/*m*),[S13] $\mathrm{SnI_4}$ (cubic, space group *Pa*–3),[S14] and $\mathrm{CsSnI_3}$ (cubic, space group *Pm*−3*m*),[S15] the following constraints must be satisfied as well.

$$\Delta\mu_\mathrm{Cs} + \Delta\mu_\mathrm{I} < \Delta H(\mathrm{CsI}) = -3.80\ \mathrm{eV}, \tag{S8}$$

$$\Delta\mu_\mathrm{Sn} + 2\Delta\mu_\mathrm{I} < \Delta H(\mathrm{SnI_2}) = -1.69\ \mathrm{eV}, \tag{S9}$$

$$\Delta\mu_\mathrm{Sn} + 4\Delta\mu_\mathrm{I} < \Delta H(\mathrm{SnI_4}) = -2.40\ \mathrm{eV}, \tag{S10}$$

$$\Delta\mu_\mathrm{Cs} + \Delta\mu_\mathrm{Sn} + 3\Delta\mu_\mathrm{I} < \Delta H(\mathrm{CsSnI_3}) = -5.77\ \mathrm{eV}. \tag{S11}$$

With all these equations satisfied, $\Delta\mu_\mathrm{Sn}$ and $\Delta\mu_\mathrm{I}$ (and, thus, $\Delta\mu_\mathrm{Cs}$ determined from Equation 4) are limited to a narrow region as shown by the yellow region defined by the A–B–C–D points in Fig. 1. Two representative chemical potential conditions in Fig. 1c, i.e., ($\Delta\mu_\mathrm{Cs}$, $\Delta\mu_\mathrm{I}$) at A (I-rich condition) and D (I-poor condition) points were chosen for the discussion.

The electronic structures for fully-relaxed SnO (tetragonal, space group *P*4/*nmm*),[S16] $\mathrm{CsSnI_3}$ (cubic, space group *Pm*−3*m*) [S15] as well as $\mathrm{Cs_2SnI_6}$ (the primitive unit cell was used), were also calculated with the HSE06 hybrid functional (α = 34%) using a 6×6×5 *k*-mesh, a 6×6×6 *k*-mesh and a 4×4×4 *k*-mesh, respectively.

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