

SUPPLEMENTARY INFORMATION

Origin of the low conversion efficiency in $\text{Cu}_2\text{ZnSnS}_4$ kesterite solar cells: the actual role of cation disorder

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Figure S1 shows the radial distribution functions $g(r)$ for the ordered kesterite, the cation-disordered special supercell, and the Monte-Carlo snapshot at 800 K. The overall agreement between the special supercell and the Monte-Carlo snapshot is demonstrated.

Figures S2 and S3 show the phase stability of $\text{Cu}_2\text{ZnSnS}_4$ under various growth conditions. The values reported in the main text refer to the growth condition P1 (Cu-poor).

Figure S4 shows the formation energies for a number of defects in $\text{Cu}_2\text{ZnSnS}_4$ under the various growth conditions given in Figs. S2 and S3.

Table S1 gives the defect concentration and hole concentration at equilibrium Fermi energy under the various growth conditions.

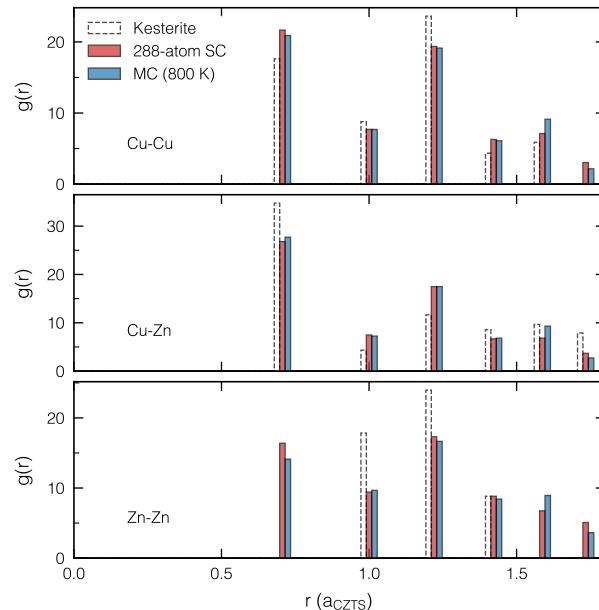


FIG. S1. Radial distribution functions $g(r)$ for the ordered kesterite, the 288-atom special supercell (SC), and the Monte-Carlo (MC) snapshot at 800 K. The bars are slightly displaced horizontally to allow for an easy comparison.

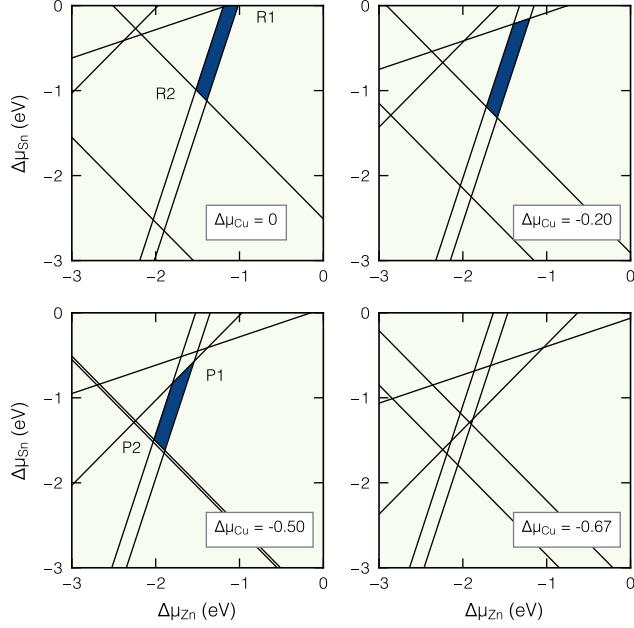


FIG. S2. Chemical potential diagrams for (cation disordered) $\text{Cu}_2\text{ZnSnS}_4$ calculated with HSE hybrid functional at varying Cu chemical potentials. The growth conditions range from Cu-rich ($\Delta\mu_{\text{Cu}} = [0, -0.20]$ eV) to Cu-poor ($\Delta\mu_{\text{Cu}} = [-0.50, -0.67]$ eV) conditions. The region where $\text{Cu}_2\text{ZnSnS}_4$ is stable is shaded. The representative boundary vertices are labeled (R1 and R2 under Cu-rich conditions, P1 and P2 under Cu-poor conditions).

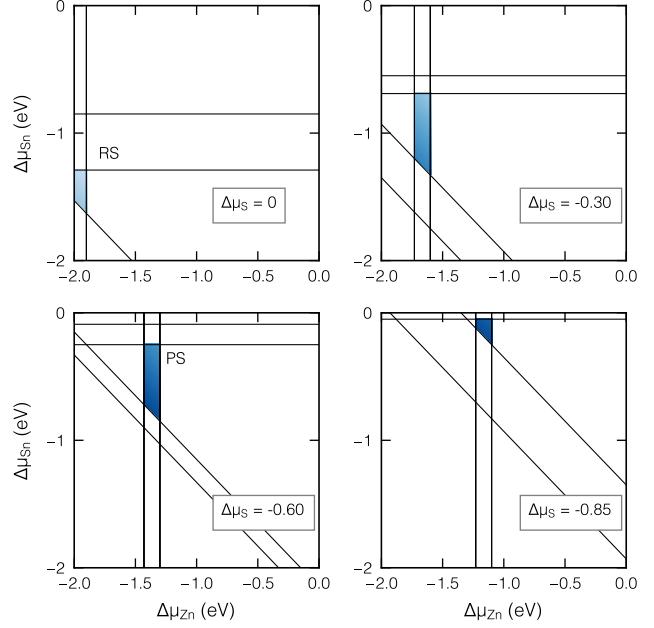


FIG. S3. Chemical potential diagrams at varying S chemical potentials. The growth conditions range from S-rich ($\Delta\mu_{\text{Cu}} = [0, -0.30]$ eV) to S-poor ($\Delta\mu_{\text{Cu}} = [-0.60, -0.85]$ eV) conditions. Two representative vertices are labeled (RS for S-rich and PS for S-poor conditions). The shade color refers to the chemical potential of Cu. Dark (bright) blue corresponds to a Cu-rich (poor) condition.

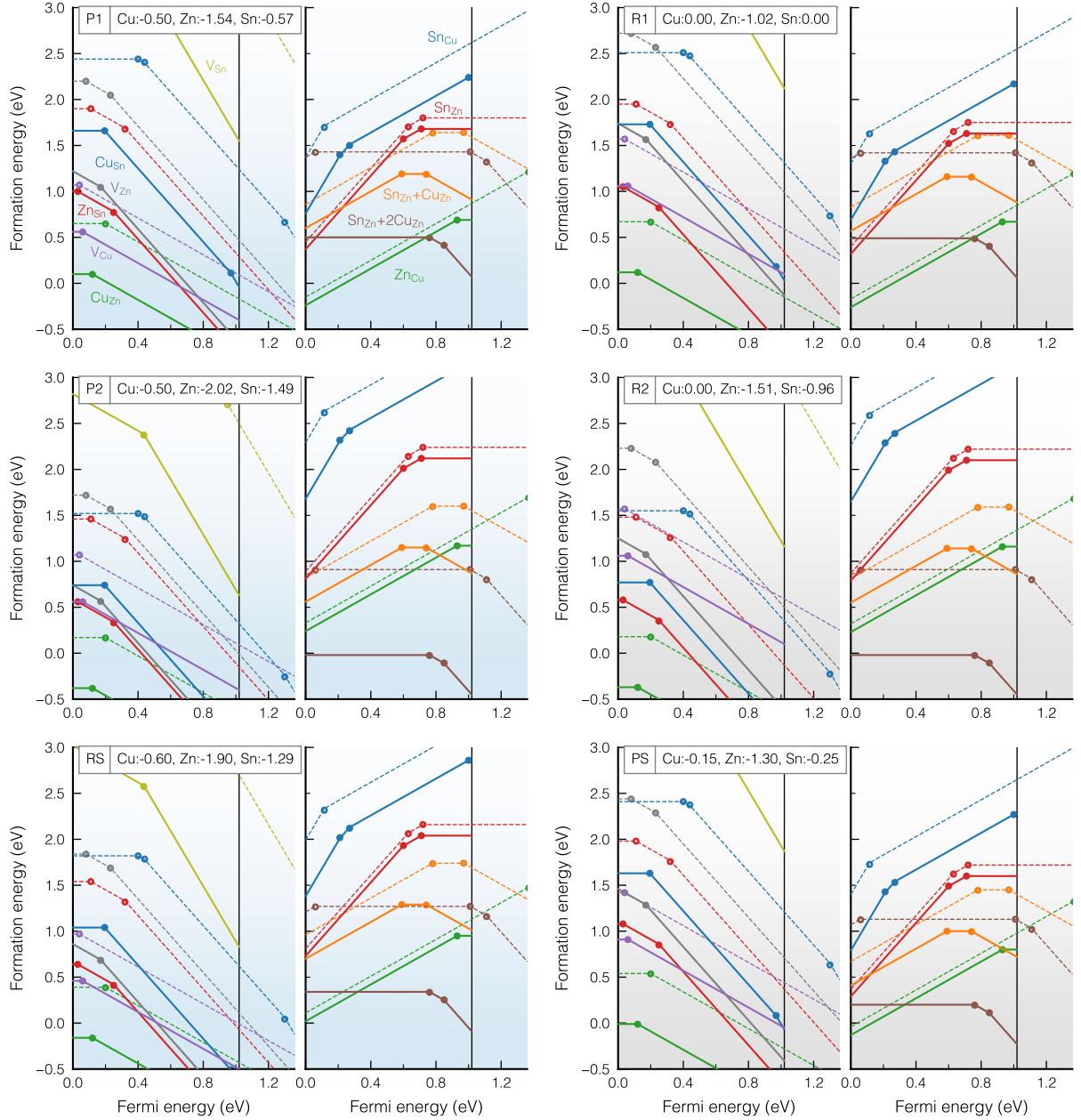


FIG. S4. Defect formation energies for $\text{Cu}_2\text{ZnSnS}_4$ obtained with HSE hybrid-functional calculations under various growth conditions (cf. Fig. S2 and S3). The results for disordered and ordered systems are shown by solid and dashed lines, respectively.

TABLE S1. Defect concentration N and hole concentration p_0 at equilibrium Fermi energy E_F (referred to the VBM) under various growth conditions for ordered and cation-disordered CZTS.

	Ordered						Disordered					
	P1	P2	R1	R2	RS	PS	P1	P2	R1	R2	RS	PS
E_F (eV)	0.52	0.05	0.54	0.05	0.26	0.41	0.25	0.00	0.27	0.00	0.00	0.14
p_0 (cm^{-3})	3×10^{10}	3×10^{18}	1×10^{10}	2×10^{18}	6×10^{14}	2×10^{12}	1×10^{15}	2×10^{19}	5×10^{14}	2×10^{19}	2×10^{19}	7×10^{16}
N (cm^{-3})												
V_{Cu}^{-1}	2×10^{18}	2×10^{15}	2×10^{15}	2×10^{12}	2×10^{17}	3×10^{15}	4×10^{19}	1×10^{18}	4×10^{16}	9×10^{14}	5×10^{18}	6×10^{16}
V_{Cu}^0	2×10^{15}	2×10^{15}	2×10^{12}	2×10^{12}	1×10^{16}	1×10^{13}	3×10^{18}	3×10^{18}	2×10^{15}	2×10^{15}	1×10^{19}	2×10^{16}
V_{Zn}^{-2}	4×10^{12}	4×10^9	4×10^9	3×10^6	4×10^{11}	5×10^9	1×10^{16}	1×10^{16}	1×10^{13}	7×10^{12}	2×10^{15}	2×10^{13}
V_{Zn}^{-1}	5×10^{10}	6×10^{10}	4×10^7	4×10^7	2×10^{11}	3×10^8	4×10^{15}	1×10^{17}	3×10^{12}	8×10^{13}	2×10^{16}	3×10^{13}
V_{Zn}^0	9×10^7	9×10^{10}	5×10^4	6×10^7	2×10^{10}	3×10^6	9×10^{13}	1×10^{17}	5×10^{10}	6×10^{13}	2×10^{16}	3×10^{12}
V_{Sn}^{-3}	7×10^{-10}	4×10^{-13}	4×10^{-13}	3×10^{-16}	3×10^{-10}	6×10^{-14}	2×10^{-3}	3×10^{-2}	1×10^{-6}	1×10^{-5}	1×10^{-3}	2×10^{-7}
V_{Sn}^{-2}	1×10^{-8}	8×10^{-9}	6×10^{-12}	5×10^{-12}	2×10^{-7}	5×10^{-12}	7×10^{-3}	3×10^0	3×10^{-6}	2×10^{-3}	2×10^{-1}	3×10^{-6}
V_{Sn}^{-1}	2×10^{-4}	1×10^{-1}	6×10^{-8}	6×10^{-5}	1×10^{-1}	3×10^{-7}	4×10^{-1}	8×10^3	2×10^{-4}	3×10^0	4×10^2	9×10^{-4}
V_{Sn}^0	1×10^{-10}	9×10^{-5}	4×10^{-14}	4×10^{-8}	5×10^{-6}	1×10^{-12}	4×10^{-4}	2×10^2	1×10^{-7}	1×10^{-1}	1×10^1	4×10^{-6}
$\text{Cu}_{\text{Zn}}^{-1}$	5×10^{19}	6×10^{19}	5×10^{19}	6×10^{19}	5×10^{19}	6×10^{19}	8×10^{21}	2×10^{23}	8×10^{21}	2×10^{23}	1×10^{22}	8×10^{21}
Cu_{Zn}^0	5×10^{17}	5×10^{20}	4×10^{17}	5×10^{20}	2×10^{19}	2×10^{18}	1×10^{21}	1×10^{24}	1×10^{21}	1×10^{24}	6×10^{22}	6×10^{21}
$\text{Cu}_{\text{Sn}}^{-3}$	6×10^2	4×10^{-1}	6×10^2	4×10^{-1}	7×10^1	9×10^0	2×10^7	3×10^8	2×10^7	2×10^8	3×10^6	3×10^5
$\text{Cu}_{\text{Sn}}^{-2}$	5×10^7	3×10^7	3×10^7	3×10^7	2×10^8	3×10^6	7×10^{11}	3×10^{14}	5×10^{11}	2×10^{14}	4×10^{12}	5×10^{10}
$\text{Cu}_{\text{Sn}}^{-1}$	2×10^7	1×10^{10}	8×10^6	7×10^9	3×10^9	5×10^6	2×10^{11}	4×10^{15}	1×10^{11}	3×10^{15}	5×10^{13}	7×10^{10}
Cu_{Sn}^0	3×10^6	2×10^{12}	1×10^6	1×10^{12}	2×10^{10}	4×10^6	2×10^{11}	1×10^{17}	6×10^{10}	6×10^{16}	1×10^{15}	2×10^{11}
$\text{Zn}_{\text{Sn}}^{-2}$	5×10^{13}	3×10^{10}	4×10^{13}	3×10^{10}	5×10^{12}	7×10^{11}	5×10^{16}	2×10^{16}	4×10^{16}	2×10^{16}	7×10^{15}	6×10^{14}
$\text{Zn}_{\text{Sn}}^{-1}$	3×10^{12}	2×10^{12}	2×10^{12}	1×10^{12}	1×10^{13}	2×10^{11}	5×10^{16}	8×10^{17}	3×10^{16}	6×10^{17}	3×10^{17}	3×10^{15}
Zn_{Sn}^0	7×10^9	4×10^{12}	3×10^9	3×10^{12}	1×10^{12}	2×10^9	2×10^{15}	1×10^{18}	1×10^{15}	1×10^{18}	4×10^{17}	7×10^{14}
Zn_{Cu}^0	3×10^{14}	2×10^{11}	3×10^{14}	3×10^{11}	6×10^{12}	5×10^{13}	4×10^{17}	4×10^{14}	6×10^{17}	5×10^{14}	1×10^{16}	8×10^{16}
$\text{Zn}_{\text{Cu}}^{+1}$	6×10^{19}	5×10^{19}	6×10^{19}	5×10^{19}	6×10^{19}	5×10^{19}	8×10^{21}	3×10^{20}	8×10^{21}	3×10^{20}	7×10^{21}	8×10^{21}
Sn_{Cu}^0	2×10^3	3×10^{-3}	4×10^3	4×10^{-3}	2×10^{-1}	1×10^3	5×10^7	8×10^1	1×10^8	1×10^2	6×10^3	3×10^7
$\text{Sn}_{\text{Cu}}^{+1}$	5×10^8	9×10^5	1×10^9	1×10^6	3×10^6	2×10^9	3×10^{12}	2×10^8	6×10^{12}	3×10^8	1×10^{10}	9×10^{12}
$\text{Sn}_{\text{Cu}}^{+2}$	1×10^6	2×10^6	2×10^6	2×10^5	1×10^7	4×10^{12}	8×10^9	6×10^{12}	1×10^{10}	6×10^{11}	6×10^{11}	6×10^{13}
$\text{Sn}_{\text{Cu}}^{+3}$	4×10^3	6×10^6	4×10^3	7×10^6	4×10^4	3×10^5	2×10^{12}	2×10^{11}	3×10^{12}	3×10^{11}	1×10^{13}	2×10^{14}
Sn_{Zn}^0	3×10^{10}	5×10^7	6×10^{10}	6×10^7	2×10^8	9×10^{10}	1×10^{11}	2×10^8	2×10^{11}	3×10^8	6×10^8	4×10^{11}
$\text{Sn}_{\text{Zn}}^{+1}$	5×10^{11}	8×10^{11}	8×10^{11}	1×10^{12}	1×10^{11}	8×10^{12}	9×10^{13}	6×10^{12}	1×10^{14}	7×10^{12}	2×10^{13}	1×10^{15}
$\text{Sn}_{\text{Zn}}^{+2}$	2×10^{12}	4×10^{15}	3×10^{12}	4×10^{15}	2×10^{13}	2×10^{14}	1×10^{16}	2×10^{16}	2×10^{16}	4×10^{16}	1×10^{17}	1×10^{18}
N (cm^{-3})												
$[\text{Sn}_{\text{Cu}} + \text{Cu}_{\text{Sn}}]^{-2}$	2×10^{-3}	2×10^{-9}	4×10^{-3}	3×10^{-9}	1×10^{-6}	9×10^{-5}	4×10^1	3×10^{-2}	8×10^1	3×10^{-2}	3×10^{-2}	2×10^0
$[\text{Sn}_{\text{Cu}} + \text{Cu}_{\text{Sn}}]^{-1}$	4×10^0	4×10^{-3}	6×10^0	5×10^{-3}	1×10^{-1}	9×10^{-1}	1×10^7	4×10^5	2×10^7	4×10^5	4×10^5	3×10^6
$[\text{Sn}_{\text{Cu}} + \text{Cu}_{\text{Sn}}]^0$	1×10^3	7×10^{11}										
$[\text{Sn}_{\text{Cu}} + \text{Cu}_{\text{Sn}}]^{+1}$	4×10^3	4×10^6	3×10^3	3×10^6	2×10^5	2×10^4	7×10^{10}	2×10^{12}	5×10^{10}	2×10^{12}	2×10^{12}	3×10^{11}
$[\text{Sn}_{\text{Zn}} + \text{Zn}_{\text{Sn}}]^{-1}$	3×10^8	3×10^5	4×10^8	4×10^5	8×10^6	7×10^7	1×10^{11}	3×10^9	2×10^{11}	3×10^9	3×10^9	2×10^{10}
$[\text{Sn}_{\text{Zn}} + \text{Zn}_{\text{Sn}}]^0$	1×10^{13}	2×10^{16}										
$[\text{Sn}_{\text{Zn}} + \text{Zn}_{\text{Sn}}]^{+1}$	4×10^9	4×10^{12}	3×10^9	4×10^{12}	2×10^{11}	2×10^{10}	1×10^{14}	5×10^{15}	1×10^{14}	5×10^{15}	5×10^{15}	7×10^{14}
$[\text{Sn}_{\text{Zn}} + \text{V}_{\text{Zn}}]^{-2}$	7×10^1	1×10^{-4}	1×10^{-1}	1×10^{-7}	4×10^{-2}	3×10^{-1}	9×10^8	1×10^6	2×10^6	1×10^3	7×10^5	3×10^6
$[\text{Sn}_{\text{Zn}} + \text{V}_{\text{Zn}}]^{-1}$	2×10^5	4×10^2	3×10^2	3×10^{-1}	5×10^3	4×10^3	3×10^{12}	1×10^{11}	4×10^9	1×10^8	8×10^{10}	6×10^{10}
$[\text{Sn}_{\text{Zn}} + \text{V}_{\text{Zn}}]^0$	1×10^8	2×10^8	1×10^5	2×10^5	1×10^8	1×10^7	4×10^{15}	8×10^{15}	5×10^{12}	6×10^{12}	4×10^{15}	4×10^{14}
$[\text{Sn}_{\text{Zn}} + 2V_{\text{Cu}}]^{-2}$	3×10^2	5×10^{-7}	6×10^{-4}	4×10^{-13}	2×10^{-2}	2×10^{-3}	1×10^4	2×10^{-2}	2×10^{-2}	1×10^{-8}	9×10^{-1}	6×10^{-2}
$[\text{Sn}_{\text{Zn}} + 2V_{\text{Cu}}]^{-1}$	1×10^7	2×10^1	2×10^1	2×10^{-5}	3×10^4	4×10^2	3×10^9	2×10^5	4×10^3	1×10^{-1}	9×10^6	8×10^4
$[\text{Sn}_{\text{Zn}} + 2V_{\text{Cu}}]^0$	7×10^{10}	1×10^8	7×10^4	8×10^1	7×10^9	8×10^6	2×10^{14}	3×10^{11}	2×10^8	2×10^5	2×10^{13}	2×10^{10}
$[\text{Sn}_{\text{Zn}} + 2\text{Cu}_{\text{Zn}}]^{-2}$	1×10^6	2×10^3	2×10^6	2×10^3	6×10^3	3×10^6	3×10^{11}	5×10^{11}	7×10^{11}	5×10^{11}	3×10^9	1×10^{12}
$[\text{Sn}_{\text{Zn}} + 2\text{Cu}_{\text{Zn}}]^{-1}$	5×10^9	1×10^{10}	8×10^9	1×10^{10}	1×10^9	8×10^{10}	2×10^{15}	1×10^{17}	3×10^{15}	1×10^{17}	6×10^{14}	3×10^{16}
$[\text{Sn}_{\text{Zn}} + 2\text{Cu}_{\text{Zn}}]^0$	6×10^{12}	1×10^{16}	7×10^{12}	1×10^{16}	6×10^{13}	5×10^{14}						