Supplemental material to "High Throughput Screening of Single Atom Co-Catalysts in $ZnIn_2S_4$ for Photocatalysis"

Md Habibur Rahman,[1)], Yujie Sun [2)] and Arun Mannodi-Kanakkithodi [1, a)]

[1]*School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907, USA*
[2]*Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221 USA*

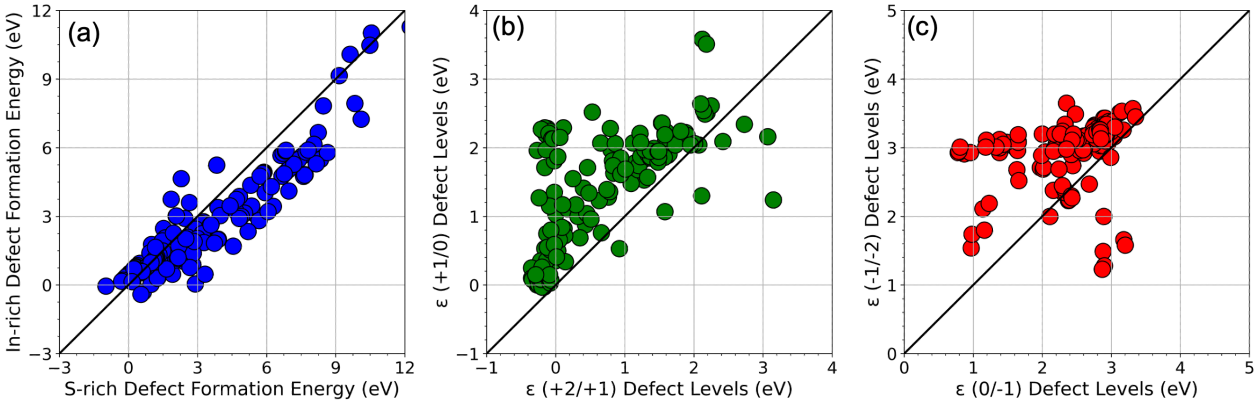

Fig. S1 Visualization of GGA+U DFT data—(a) Cation (In) vs anion(S) defect rich formation energy, (b) +2/+1 vs +1/0 and (c) 0/-1 vs -1/-2 defect levels.

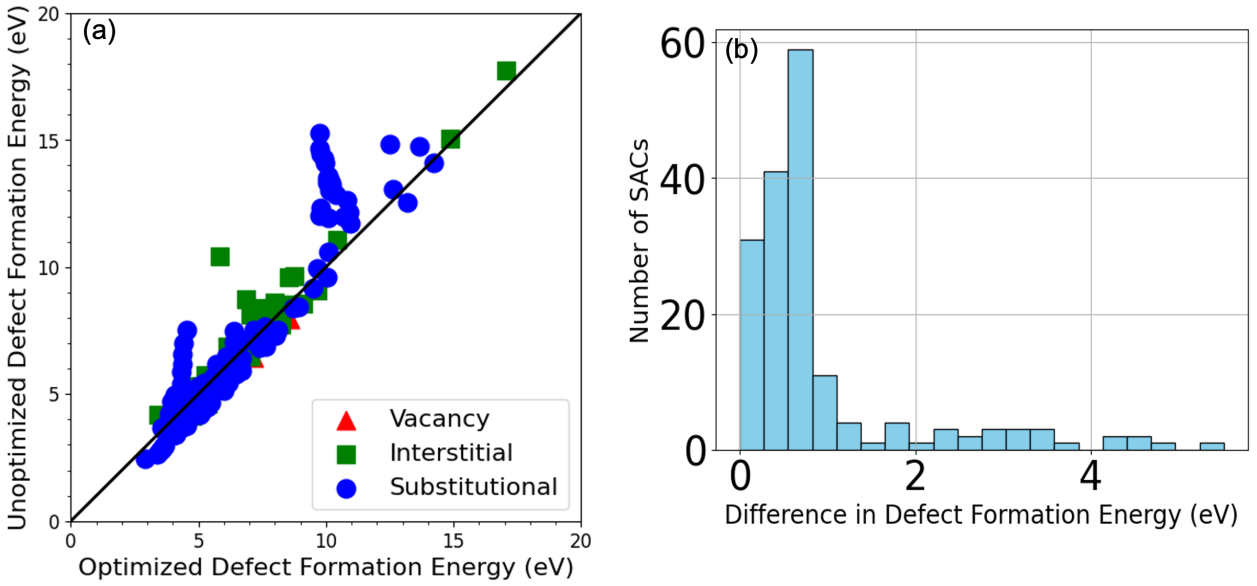

Fig. S2 (a) DFT optimized vs unoptimized defect formation energy (DFE) (b) Distribution of DFE difference (DFT optimized – DFT unoptimized) for SACs.

A Chemical Potential Expressions for SACs

[a]amannodi@purdue.edu

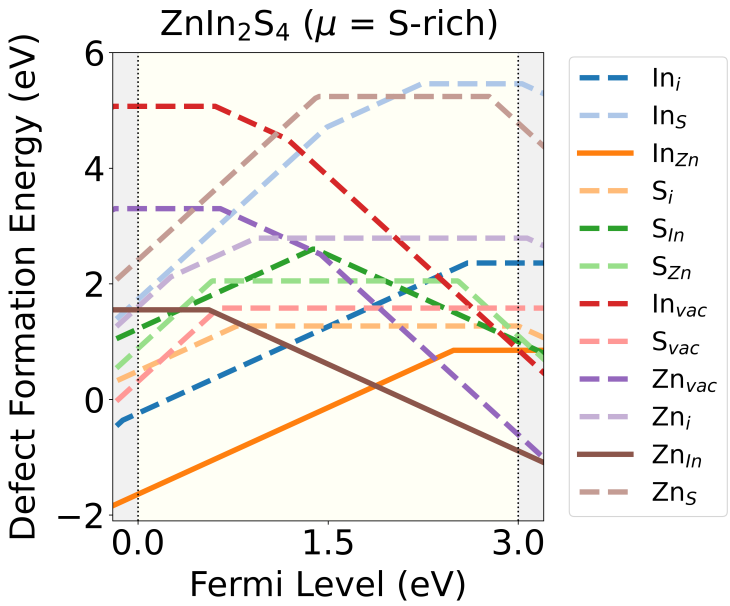

Fig. S3 DFE of all the native defects in ZIS as a function of E_F using HSE06 functional under S-rich conditions. The lowest energy donor and acceptor are depicted with solid line.

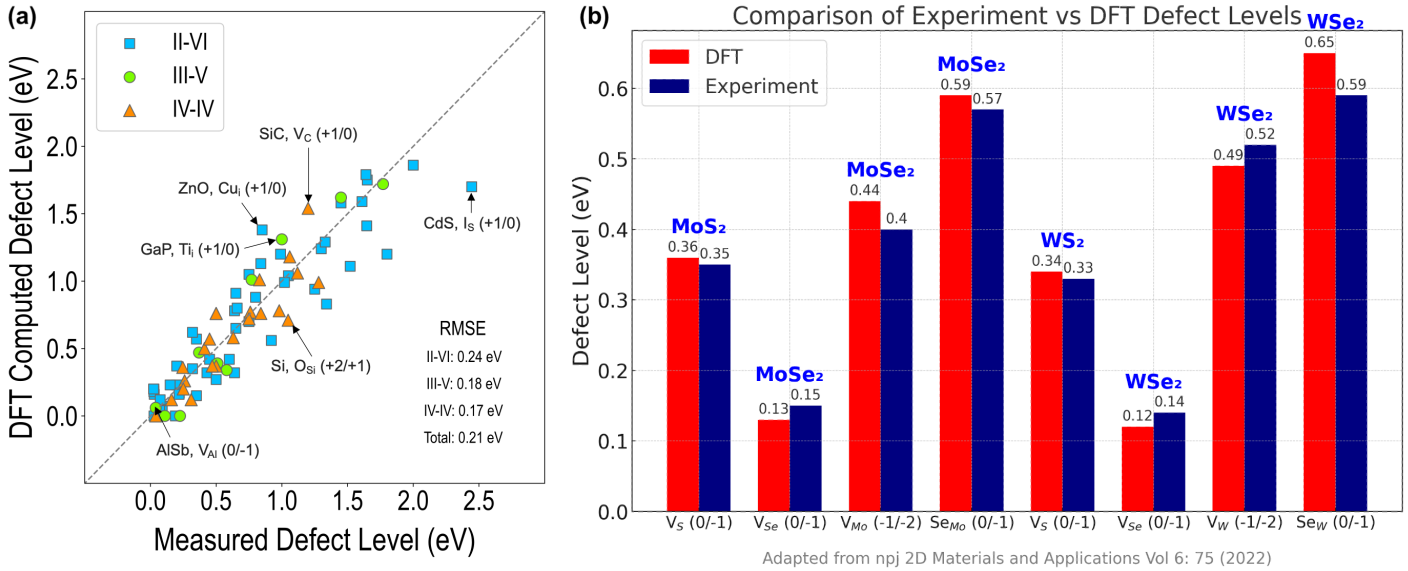

Fig. S4 Comparison of defect levels between DFT calculations and experimental observations for various (a) binary zinc blende (ZB) semiconductors and (b) transition metal dichalcogenide (TMDC) semiconductors. Collected from prior literature[52,53]. Permission to reuse Fig. S4(a) has been obtained from Elsevier.

$$\Delta\mu_{Sc} + 2\Delta\mu_S = \Delta H(ScS_2) \qquad \Delta\mu_{Cr} + 2\Delta\mu_S = \Delta H(CrS_2) \qquad \Delta\mu_{Co} + 2\Delta\mu_S = \Delta H(CoS_2)$$

$$\Delta\mu_{Ti} + 2\Delta\mu_S = \Delta H(TiS_2) \qquad \Delta\mu_{Mn} + 2\Delta\mu_S = \Delta H(MnS_2) \qquad \Delta\mu_{Ni} + 2\Delta\mu_S = \Delta H(NiS_2)$$

$$\Delta\mu_{V} + 2\Delta\mu_S = \Delta H(VS_2) \qquad \Delta\mu_{Fe} + \Delta\mu_S = \Delta H(FeS) \qquad \Delta\mu_{Cu} + \Delta\mu_S = \Delta H(CuS)$$

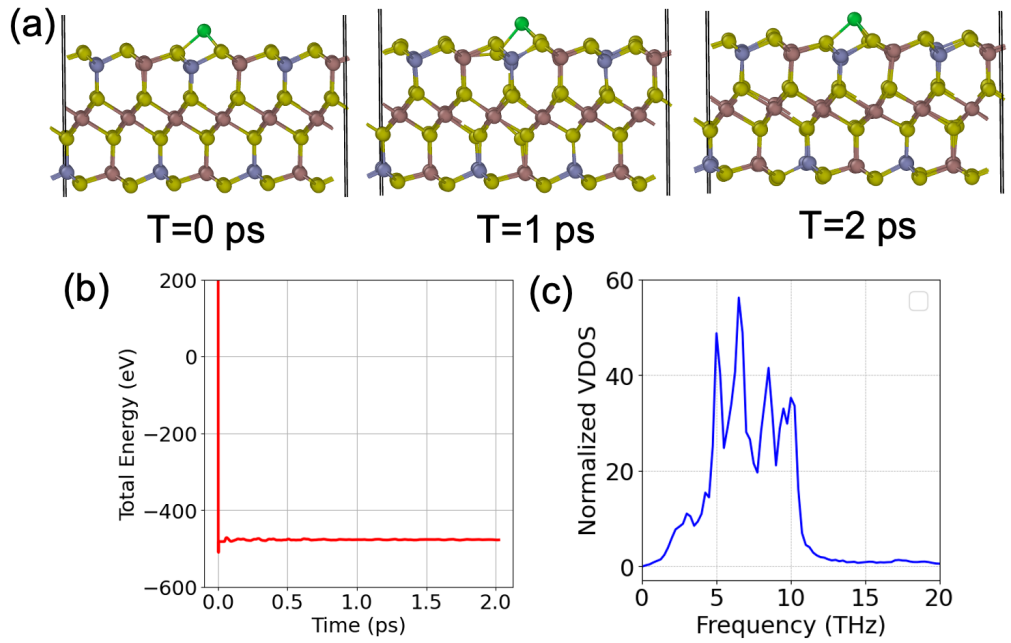

Fig. S5 (a) Snapshots of the crystal structure of Yb_i (green color) in ZIS during AIMD simulations at 300 K. (b) Energy profile during the AIMD simulation. (c) Normalized vibrational density of states (VDOS) for Yb_i in ZIS.

$$\Delta\mu_{Y}+\Delta\mu_{S}=\Delta H(YS)$$

$$\Delta\mu_{Zr}+\Delta\mu_{S}=\Delta H(ZrS)$$

$$\Delta\mu_{Nb}+3\Delta\mu_{S}=\Delta H(NbS_3)$$

$$\Delta\mu_{Mo}+2\Delta\mu_{S}=\Delta H(MoS_2)$$

$$\Delta\mu_{Tc}+2\Delta\mu_{S}=\Delta H(TcS_2)$$

$$\Delta\mu_{Ru}+2\Delta\mu_{S}=\Delta H(RuS_2)$$

$$\Delta\mu_{Rh}+2\Delta\mu_{S}=\Delta H(RhS_2)$$

$$\Delta\mu_{Pd}+2\Delta\mu_{S}=\Delta H(PdS_2)$$

$$2\Delta\mu_{Ag}+\Delta\mu_{S}=\Delta H(Ag_2S)$$

$$\Delta\mu_{Cd}+\Delta\mu_{S}=\Delta H(CdS)$$

$$\Delta\mu_{La}+\Delta\mu_{S}=\Delta H(LaS)$$

$$\Delta\mu_{Ce}+\Delta\mu_{S}=\Delta H(CeS)$$

$$\Delta\mu_{Pr}+\Delta\mu_{S}=\Delta H(PrS)$$

$$\Delta\mu_{Nd}+\Delta\mu_{S}=\Delta H(NdS)$$

$$\Delta\mu_{Pm}+\Delta\mu_{S}=\Delta H(PmS)$$

$$\Delta\mu_{Sm}+\Delta\mu_{S}=\Delta H(SmS)$$

$$\Delta\mu_{Eu}+\Delta\mu_{S}=\Delta H(EuS)$$

$$\Delta\mu_{Gd}+\Delta\mu_{S}=\Delta H(GdS)$$

$$\Delta\mu_{Tb}+\Delta\mu_{S}=\Delta H(TbS)$$

$$\Delta\mu_{Dy}+\Delta\mu_{S}=\Delta H(DyS)$$

$$\Delta\mu_{Ho}+\Delta\mu_{S}=\Delta H(HoS)$$

$$\Delta\mu_{Er}+\Delta\mu_{S}=\Delta H(ErS)$$

$$\Delta\mu_{Tm}+\Delta\mu_{S}=\Delta H(TmS)$$

$$\Delta\mu_{Yb}+\Delta\mu_{S}=\Delta H(YbS)$$

$$\Delta\mu_{Lu}+\Delta\mu_{S}=\Delta H(LuS)$$

$$2\Delta\mu_{Hf}+\Delta\mu_{S}=\Delta H(Hf_2S)$$

$$3\Delta\mu_{Ta}+2\Delta\mu_{S}=\Delta H(Ta_3S_2)$$

$$\Delta\mu_{W}+2\Delta\mu_{S}=\Delta H(WS_2)$$

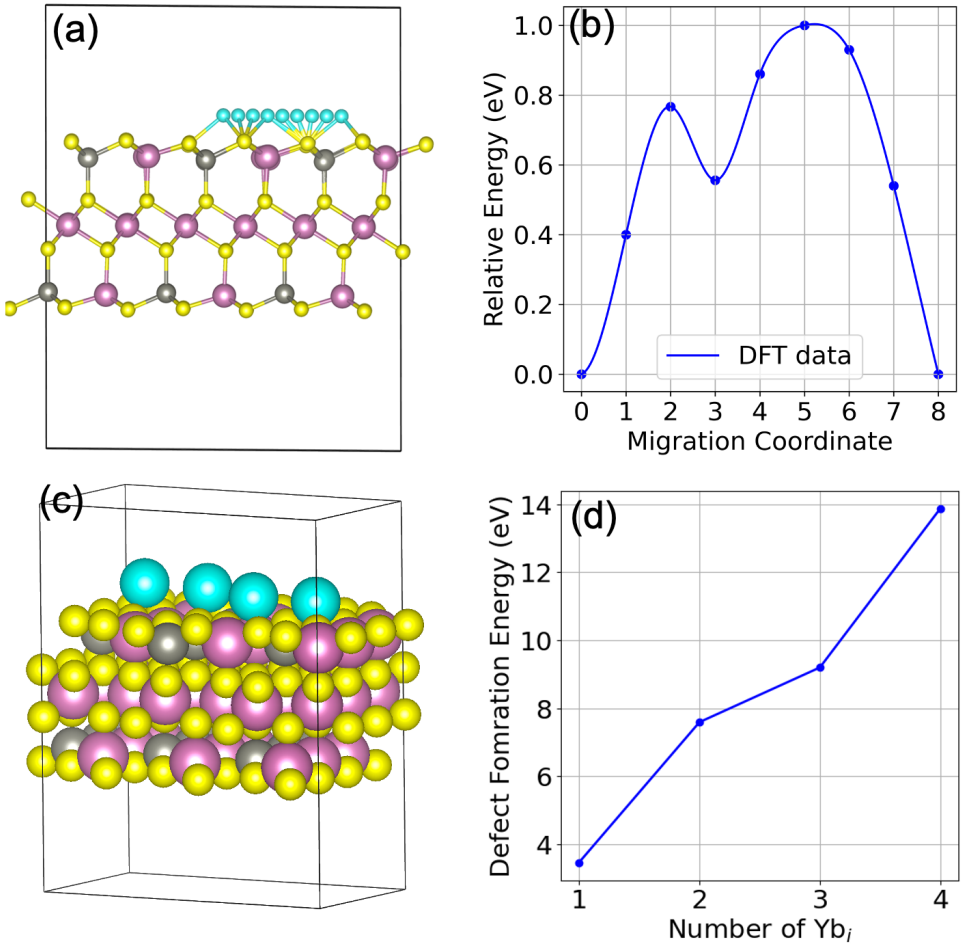

Fig. S6 (a) Diffusion profile of Yb_i SAC in ZIS simulated through DFT, (b) DFT calculated migration energy barrier of the same SAC as a function of migration coordinate, (c) cluster of Yb_i (quadruple) SACs in ZIS, (d) defect formation energy of single, double, triple, and quadruple SACs. Color scheme: In (Pink), Zn (Silver), S (Yellow), and Yb (Cyan). .

$$\Delta\mu_{Re} + 2\Delta\mu_S = \Delta H(ReS_2)$$

$$\Delta\mu_{Ir} + 2\Delta\mu_S = \Delta H(IrS_2)$$

$$2\Delta\mu_{Au} + \Delta\mu_S = \Delta H(Au_2S)$$

$$\Delta\mu_{Os} + 2\Delta\mu_S = \Delta H(OsS_2)$$

$$\Delta\mu_{Pt} + 2\Delta\mu_S = \Delta H(PtS_2)$$

$$\Delta\mu_{Hg} + \Delta\mu_S = \Delta H(HgS)$$

Table SI Gibbs Free Energy of SACs

Defects	Gibbs Free Energy (eV)
Sc_{In}	2.06
Ti_{In}	0.61
Co_{In}	0.50
Y_{In}	2.14
Zr_{In}	0.37
Cd_{In}	0.64
La_{In}	2.20
Ce_{In}	1.31
Pr_{In}	2.18
Nd_{In}	2.18
Pm_{In}	2.16
Sm_{In}	2.16
Eu_{In}	0.63
Gd_{In}	2.14
Tb_{In}	2.14
Dy_{In}	2.13
Ho_{In}	2.12
Er_{In}	2.12
Tm_{In}	2.11
Yb_{In}	1.06
Lu_{In}	2.10
Hf_{In}	0.32
Ta_{In}	0.30
Hg_{In}	0.91
Sc_{Zn}	0.97
Mn_{Zn}	1.04
Ni_{Zn}	0.49
Y_{Zn}	0.92
Tc_{Zn}	0.17
Cd_{Zn}	2.27
La_{Zn}	0.81
Ce_{Zn}	0.85
Pr_{Zn}	0.83
Nd_{Zn}	0.86
Pm_{Zn}	0.89
Sm_{Zn}	0.90
Eu_{Zn}	2.20
Gd_{Zn}	0.92
Tb_{Zn}	3.37
Dy_{Zn}	3.37
Ho_{Zn}	3.37
Er_{Zn}	0.94
Tm_{Zn}	0.95
Yb_{Zn}	2.20
Lu_{Zn}	0.95
Hg_{Zn}	2.20
Ag_{S}	3.08
Au_{S}	0.19
Cu_{i}	0.95
Y_{i}	0.91
Ag_{i}	2.81
La_{i}	0.20
Nd_{i}	6.42
Eu_{i}	0.24
Gd_{i}	0.65
Tm_{i}	0.93
Yb_{i}	0.07
Hf_{i}	1.12
Au_{i}	0.30
Hg_{i}	0.93