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Supplementary Information for:

First-principles study of intrinsic and hydrogen point defects in the earth-abundant photovoltaic absorber Zn_3P_2

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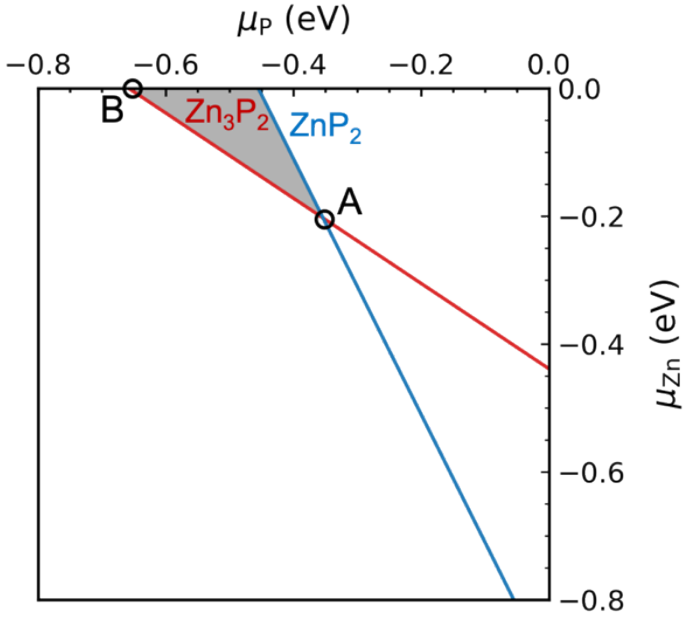

Fig. S1 Calculated chemical-potential region (gray colored) for which compositionally stoichiometric Zn_3P_2 is thermodynamically stable. This region prevents formation of the secondary phase ZnP_2 (indicated by the blue line) and bulk Zn and P phases. Two different chemical-potential points: A (μ_{Zn} =− 0.203 eV, μ_P =− 0.354 eV) and B (μ_{Zn} = 0.0 eV, μ_P =− 0.658 eV), which represent Zn-poor (P-rich) and Zn-rich (P-poor) equilibrium growth conditions, respectively, are chosen for computing the defect formation energies.

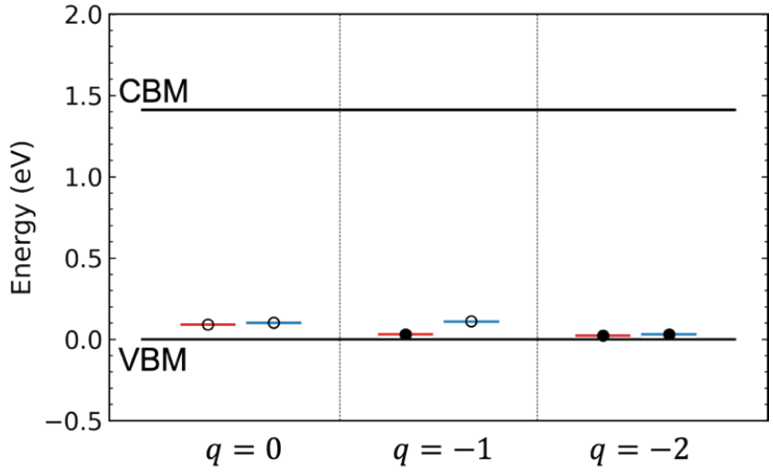

Fig. S2 Single-particle defect states of the V_{Zn} in three different charge states: $q = 0$, -1, and -2. The filled and empty dots indicate the occupied and unoccupied defect states in the spin-up (red) and spin-down (blue) channels.

Table S1 Thermodynamic transition levels between different charge states q and q' for the intrinsic point defects and the H-related point defects in Zn_3P_2. Results from previous calculations by Demers *et al*. (Ref. 1) and Yin *et al*. (Ref. 2) are included for comparison.

Defect	$\epsilon(q/q')$
V_{Zn}	0.11 $(0/-)$, 0.23 $(-/2-)$
V_{Zn} (Refs. [1, 2])	0.06[a] 0.4[b] $(0/-)$, 0.09[a] 0.75[b] $(-/2-)$
V_P	0.88 $(+/-)$, 1.04 $(+/0)$, 0.71 $(0/-)$
V_P (Refs. [1, 2])	0.25[b] $(2+/+)$, 0.24[a] 0.75[b] $(+/0)$
Zn_i	0.72 $(2+/+)$, 0.95 $(+/0)$
Zn_i (Refs. [1, 2])	0.04[a] 0.87[b] $(2+/+)$, 0.06[a] 1.22[b] $(+/0)$
P_i	0.17 $(3+/0)$, 0.69 $(0/-)$
P_i (Refs. [1, 2])	0.30[a] 0.35[b] $(0/-)$, 0.96[b] $(-/2-)$
Zn_P	0.22 $(3+/2+)$, 0.49 $(2+/+)$, 0.43 $(2+/0)$, 0.38 $(+/0)$, 1.26 $(0/2-)$
P_{Zn}	0.24 $(3+/+)$, 0.72 $(+/0)$, 0.61 $(+/-)$, 0.50 $(0/-)$
H_i	0.57 $(+/-)$
$H + V_{Zn}$	0.09 $(0/-)$
$2H + V_{Zn}$	None
$H + V_P$	0.13 $(+/0)$

a Yin *et al*.
b Demers *et al*.

Table S2 Convergence tests using an energy cutoff of 500 eV or a larger $3 \times 3 \times 2$ supercell. The calculations using 400 eV cutoff and $2 \times 2 \times 2$ supercell have been reported in the main text. For the test calculations, the supercells are based on the same primitive unit-cell lattice parameters, but internal atomic positions are relaxed under the same force convergence criterion. A Γ-only **k**-point is used throughout for Brillouin-zone sampling.

Transition level	400 eV cutoff, $2 \times 2 \times 2$ supercell	500 eV cutoff, $2 \times 2 \times 2$ supercell	400 eV cutoff, $3 \times 3 \times 2$ supercell
V_{Zn} $(0/-)$	0.11	0.11	0.08
V_{Zn} $(-/2-)$	0.23	0.23	0.18
P_i $(0/-)$	0.69	0.70	0.75

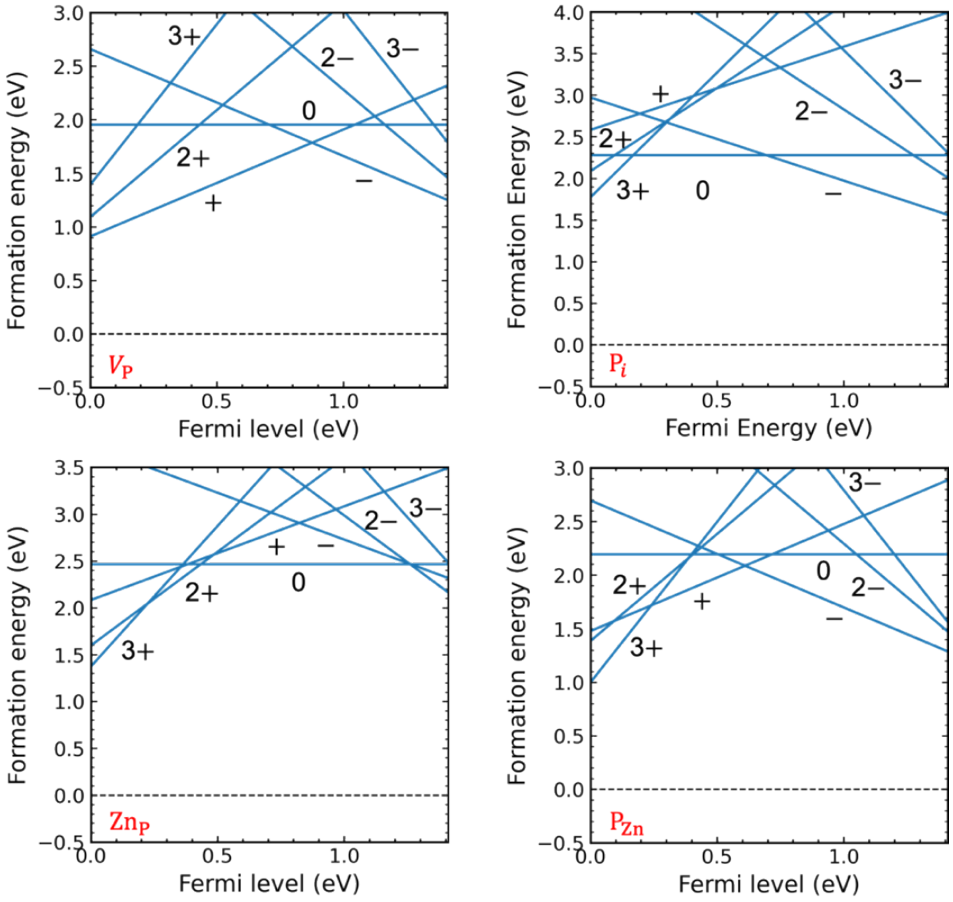

Fig. S3 Formation energies of the ^{V_P}, ^{P_i}, ^{Zn_P}, and $^{P_{Zn}}$ as a function of Fermi level with more detailed information on charge-state transitions.

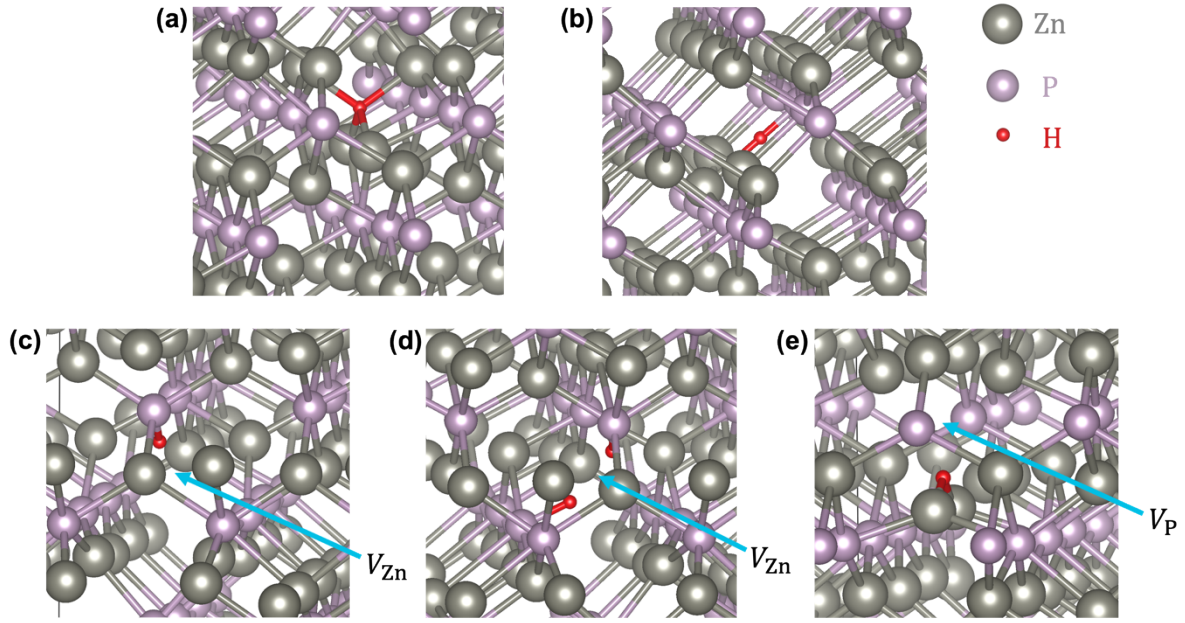

Fig. S4 Local atomic geometry: (a) ^{H_i} in $q = 0$ and -1 charge states; (b) ^{H_i} in $q = +1$ charge states; (c)-(e) $^{H + V_{Zn}}$, $^{2H + V_{Zn}}$, and $^{H + V_P}$ complexes (in their neutral charge state) in Zn_3P_2. For eye guide the vacancy centers are pointed by arrows.

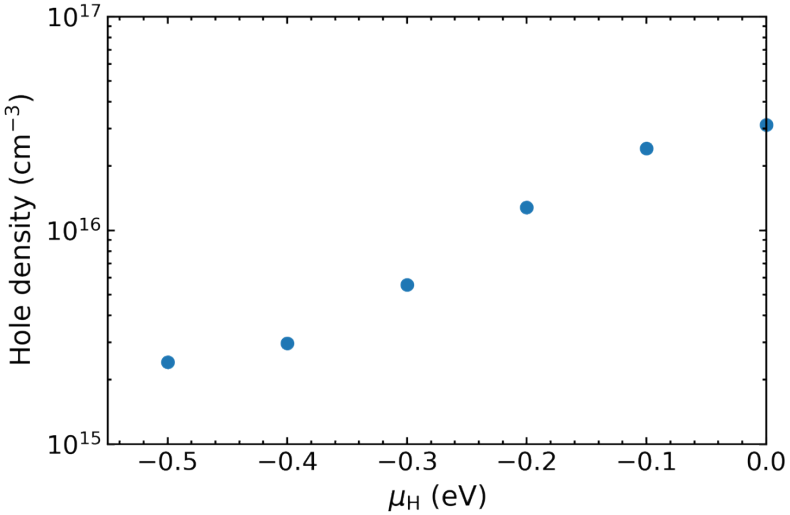

Fig. S5 Calculated bulk hole density in Zn_3P_2 as a function of hydrogen chemical potential (μ_H), assuming the V_{Zn} concentration is not affected by hydrogen. $\mu_H = 0$ corresponds to the H-rich limit. For μ_H higher (lower) than ~0.4 eV, hole carriers arise mostly from the $H + V_{Zn}$ (V_{Zn}) acceptors. In calculating the defect and carrier densities, the temperature is set to 350 ℃ (a typical growth temperature of Zn_3P_2).[3]

References

1. S. Demers and A. van de Walle, *Physical Review B*, 2012, **85**, 195208.
2. W.-J. Yin and Y. Yan, *Journal of Applied Physics*, 2013, **113**, 013708.
3. K. Kakishita, S. Ikeda and T. Suda, *Journal of Crystal Growth*, 1991, **115**, 793-797.