

Role of Na and Ca as Isovalent Dopants in Cu₂ZnSnS₄ Solar Cells

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ABSTRACT: A pathway to improve the efficiency of Cu₂ZnSnS₄ (CZTS)-based solar cells, which form an important class of beyond-Si, thin-film photovoltaic technology, is the employment of sustainable isovalent dopants (substituting for Cu and Zn) to suppress formation of disorder-inducing, performance-limiting antisite defects. Using calculations based on density functional theory, we examine the influence of Na and Ca as isovalent dopants for Cu and Zn, respectively, on defect formation, thermodynamic stability, and electronic properties of CZTS. On the basis of defect formation energies, we find that Na-doping should be feasible within CZTS while the incorporation of Ca will be difficult. Importantly, both Na and Ca effectively mitigate formation of antisites that cause disorder, if incorporated



within the CZTS structure, across doping and Cu-chemical-potential conditions. Thermodynamically, doping high concentrations of Na into CZTS will result in phase separation between CZTS and Na_2ZnSnS_4 domains, whereas large additions of Ca will lead to formation of other secondary phases, such as Cu₂SnS₃ and CaS. With respect to electronic properties, Na (Ca) doping should cause a significant (marginal) increase in the band gap of kesterite CZTS. Overall, we suggest low Na-doping in CZTS as a promising pathway to improve performance of CZTS-based solar cells.

KEYWORDS: Solar cells, Cu_2ZnSnS_{4} , Isovalent doping, Defect formation, Density functional theory

INTRODUCTION

The demand for energy in our modern world is constantly increasing, with an urgent need to use more clean and sustainable methods to produce electricity than using fossil fuels. One of the key technologies that meets this requirement is photovoltaic (PV) cells, which convert incoming solar irradiation into electricity. Current state-of-the-art PVs are manufactured using multicrystalline Si, with peak photoconversion efficiencies >20%.^{1,2} However, Si PVs suffer from poor light absorption due to Si's indirect band gap, which is partly overcome by utilizing thicker solar cells.^{3,4} Thin-film solar cells,⁵ such as those based on Cu_2ZnSnS_4 (CZTS),⁶ which employ a direct band gap semiconductor with significantly improved light absorption, present a promising alternative to Si PVs.

Importantly, CZTS is made of cheap, abundant, and nontoxic elements and is environmentally friendly to process,⁷ unlike other semiconductors that have been employed in thinfilm cells, such as GaAs,⁸ CdTe,⁹ Cu(In,Ga)(S,Se)₂,¹⁰ and Pbbased perovskites.¹¹ Additionally, CZTS exhibits a direct band gap of $\sim 1.4-1.6$ eV,^{6,12} which is optimal for PV applications. However, CZTS-based solar cells, so far, have shown relatively poor efficiencies ($<13\%^{13-15}$), which have been attributed to the presence of Cu-Zn antisite defects¹⁶⁻²³ that induce disorder in the CZTS structure²⁴ resulting in band gap narrowing and poor light absorption. Antisite formation in CZTS is also aided by the near-degeneracy of the kesterite and

stannite polymorphs that CZTS can adopt.^{23,25} Prior theoretical and experimental work has shown that the use of isovalent dopants that exhibit ionic radii significantly different from Cu and Zn can inhibit disorder-inducing antisite formation and improve the performance of CZTS cells.^{23,26} Indeed, the introduction of Ag and Cd into CZTS, under select doping conditions, improves both the open-circuit voltage $(V_{\rm oc})$ and the photoconversion efficiency.^{27–32} Given that Ag is rare and Cd is toxic, it is preferable to identify effective, sustainable dopants, such as isovalent alkali and alkaline-earth metals.

In this work, we use density functional theory $(DFT)^{33,34}$ based calculations to explore the impact of doping Na (isovalent with Cu) and Ca (isovalent with Zn) on the antisite formation, bulk stability, and electronic properties of CZTS. Our choice of Na and Ca is primarily motivated from their corresponding ionic radii, namely 0.99 Å for Na⁺ in tetrahedral coordination and 1.02 Å for Ca2+, similar to Ag+ (1.0 Å) and Cd²⁺ (0.95 Å) in similar coordination environments.³⁵ Our results indicate that both Na and Ca, if successfully incorporated into the CZTS lattice, can efficiently suppress disorder-inducing antisites across doping concentrations and Cu chemical potentials. On the basis of our



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Figure 1. (Top panel) The kesterite structure (left) of pristine Cu_2ZnSnS_4 , which forms $Cu_{Zn}+Zn_{Cu}$ antisites resulting in a defective kesterite structure (middle). Eventually, high concentrations of $Cu_{Zn}+Zn_{Cu}$ can produce the stannite polymorph (right). (Bottom panel) The stable Na–Cu ordering within the kesterite unit cell at 25%, 50%, and 75% Na is displayed, alongside the Ca–Zn ordering at 50% Ca. Blue, gray, green, yellow, red, and purple spheres indicate Cu, Zn, Sn, S, Na, and Ca atoms, respectively. Dotted black lines in all structures corresponds to the conventional cell of kesterite or stannite.

estimates of the stability of CZTS under various Na- and Cadoping concentrations, we find that doping large quantities of Na is likely to induce phase separation into CZTS and Na₂ZnSnS₄ (NZTS) domains, while high concentrations of Ca will result in the formation of decomposition products. Additionally, Na incorporation should cause a significant increase in the band gaps of both the kesterite and stannite polymorphs, while Ca's impact is likely marginal on the band gap of kesterite CZTS. Finally, combining our predictions on defect formation, stability, and band gaps, we identify doping low concentrations of Na into the CZTS lattice as a promising pathway to improve efficiencies, whereas Ca-incorporation probably will be difficult.

METHODS

To calculate defect formation energies, stabilities, and band gaps, we used spin-polarized DFT as implemented in the Vienna ab initio simulation package (VASP).^{36,37} We used a kinetic energy cutoff of 520 eV for the plane wave basis and also employed the all-electron, frozen-core projector augmented wave (PAW)³⁸ theory. We sampled the Brillouin zone on a dense mesh of at least 1728 *k*-points per reciprocal atom,^{23,39} which converges the total energies to within 0.05 meV/atom.²³ We used the strongly constrained appropriately normed (SCAN)⁴⁰ functional for describing the electronic exchange-correlation (XC) interactions in all our bulk and

defect calculations since SCAN satisfies all the 17 known constraints for an XC functional⁴¹ and a previous study demonstrated SCAN to accurately predict defect and bulk energetics within CZTS.²³ However, it is also known that SCAN does not provide robust qualitative predictions for band gaps,^{23,42} which motivated us to use a generalized gradient approximation $(GGA)^{43}$ functional with a Hubbard U^{44} term added on transition-metal atoms alongside dispersion (D) corrections,⁴⁵ resulting in a GGA+U+D functional^{22,25} used for optimizing structures, and then the GGA+U functional was used in a non-self-consistent calculation to assess band gaps. Specifically, we used U = 3.6, 4.5, and 4.8 eV for Cu, Zn, and Sn, respectively, as determined previously⁴⁶ using electrostatically embedded unrestricted Hartree-Fock calculations.⁴⁷ In all calculations, the total energy and the atomic forces were converged to within 0.01 meV and |0.03| eV/Å, respectively. Throughout this paper, we use the Kröger–Vink notation⁴⁸ to represent defects, where x_y indicates a defect with species x on a y-site. Thus, Cu_{7n} represents an antisite with Cu occupying a Zn-site.

Structure. At equilibrium, the stable polymorph (i.e., the ground state) of CZTS is kesterite, as displayed in the top left panel of Figure 1, where all cations are tetrahedrally coordinated by S atoms (and vice versa). Notably, the kesterite structure readily forms $Cu_{Zn}+Zn_{Cu}$ antisites, as highlighted by the red arrows and boxes in Figure 1, leading to the formation of a defective (or disordered) structure (top center, Figure 1).



Figure 2. Formation energies of various defects, calculated with DFT-SCAN, are plotted against Cu chemical potential under low Na (0.75 at.%, $Cu_{1.9}Na_{0.06}ZnSnS_4$, panel a) and high Na (6.25 at.%, $Cu_{1.5}Na_{0.5}ZnSnS_4$, panel b) doping conditions. Dotted vertical green lines correspond to the various Cu-conditions considered. The orange band in each panel reflects the formation energy of disorder-inducing antisites in undoped-Cu₂ZnSnS₄. The "(Sn)" and "(Zn)" text notations reflect defect formation on Cu-sites on the Sn- and Zn-planes, respectively, of the kesterite structure. Note that at.% of dopant is normalized per formula unit of Cu_2ZnSnS_4 .

Eventually, a significant concentration of $Cu_{Zn}+Zn_{Cu}$ antisites will produce the stannite structure (top right, Figure 1), which exhibits a less than ideal band gap for PV applications.^{23,24} The primary difference between the kesterite and stannite structures is the stacking of cations along the [001] direction, with Sn (+Cu) and Zn (+Cu) planes in kesterite and Zn+Sn and Cu planes in stannite, as highlighted by the text notation "Sn", "Zn", "Zn+Sn", and "Cu", respectively, in Figure 1.

While introducing intermediate to high concentrations of dopants in CZTS (~25% to 75%, bottom panel of Figure 1), several configurations of arranging the dopant within the kesterite unit cell are possible. For example, 25% Na-doping within the kesterite unit cell leads to 4 distinct configurations, where the Na atom substitutes exactly one of the four Cu atoms. Thus, we calculated the energies of all symmetry-distinct configurations at 25%, 50%, and 75% Na (red spheres) and at 50% Ca (purple spheres) using DFT-SCAN, with Figure 1 (bottom panel) displaying the lowest energy configurations, which then are used for any defect and/or stability evaluations (vide infra).

Defect Formation Energies and Thermodynamic Stabilities. The formation energy of any defect is given by the following equation

$$E_{\text{defect}}^{\text{formation}} = E_{\text{bulk}}^{\text{defective}} - E_{\text{bulk}}^{\text{pristine}} + \Sigma_i n_i \mu_i + q E_F$$
$$+ E_{\text{corr}} \tag{1}$$

 $E_{\text{bulk}}^{\text{defective}}$, $E_{\text{bulk}}^{\text{pristine}}$, n_i and μ_i refer to the energy of bulk CZTS with the defect, the energy of pristine bulk CZTS, the number of atoms of species *i* that are added (<0) or removed (>0) to form the defect, and the chemical potential of species *i*, respectively. While we consider the formation of only neutral defects (q = 0) in our calculations, for charged (or ionized) defects, the formation energy also depends on the Fermi level (E_F) across the band gap and electrostatic corrections (E_{corr}) to account for any spurious interactions of ionized defects with its periodic images.^{49,50} Similar to a previous study,²³ we calculate

defect formation energies in a 2 × 2 × 2 supercell of CZTS and as a function of Cu chemical potential (μ_{Cu}). Also, we consider three distinct chemical scenarios:²³ (i) Cu-rich: bulk CZTS is in equilibrium with metallic-Cu, ZnS, and SnS, representing Cu-, Zn-, and Sn-rich conditions; (ii) constrained Cu-poor: CZTS is in equilibrium with Cu-deficient phases and ZnS and SnS, signifying Cu-poor, Zn-rich, and Sn-rich conditions; and (iii) Cu-poor: lowest possible μ_{Cu} that CZTS is stable at without any additional constraints.

We calculate the absolute values of chemical potentials by constructing quinary Cu-Zn-Sn-S-Na and Cu-Zn-Sn-S-Ca phase diagrams at 0 K, based on DFT-SCAN calculations of available binary, ternary, quaternary, and quinary structures²³ in the inorganic crystal structure database (ICSD),⁵¹ using the python materials genomics (pymatgen)⁵² toolkit. The chemical potential of the dopant (e.g., μ_{Ca}) is determined by the Gibbs free energy of formation of the dopant-containing phase exhibiting the highest μ_{dopant} (e.g., $\Delta G_f^{CaS} = \mu_{Ca} + \mu_S$), given the constraints on the Cu, Zn, and Sn chemical potentials described above and the required stability of bulk CZTS (i.e., $\Delta G_f^{CZTS} = 2 \mu_{Cu} + \mu_{Zn} + \mu_{Sn} + 4 \mu_S$). The 0 K phase diagrams, or the convex hulls of lowest energy structures, are subsequently used to evaluate the thermodynamic stability of Na- and Ca-doped CZTS at various doping concentrations. Specifically, for each composition (and/or structure), we calculate the energy above the convex hull (E^{hull}) at 0 K, which is the energy released upon decomposition to stable phases at that composition. Mathematically, E^{hull} is the distance away from the convex hull at a given composition. Note that values of E^{hull} are always positive: a thermodynamically stable phase at any temperature will have $E^{\text{hull}} = 0$, while $E^{\text{hull}} > 0$ indicates metastability. Note that E^{hull} is strictly an energetic contribution, and entropic contributions (vibrational entropy for solids ~0.026 eV/atom at 298 $K^{53,54}$) at higher temperatures may stabilize metastable phases.



Figure 3. Formation energies of various defects, calculated with DFT-SCAN, are plotted against Cu chemical potential under low Ca (0.75 at.%, $Cu_2Zn_{0.94}Ca_{0.06}SnS_4$, panel a) and high Ca (6.25 at.%, $Cu_2Zn_{0.5}Ca_{0.5}SnS_4$, panel b) doping conditions. Dotted vertical green lines correspond to the various Cu-conditions considered. The orange band in each panel reflects the formation energy of disorder-inducing antisites in undoped-Cu_2ZnSnS_4. The "(Sn)", "(Zn)", and "(Ca)" text notations reflect defect formation on Cu-sites on the Sn-, Zn-, and Ca-planes, respectively, of the kesterite structure. Note that at.% of dopant is normalized per formula unit of Cu_2ZnSnS_4 .

RESULTS AND DISCUSSION

Defects with Na-Doping. Figure 2 displays the defect formation energies, calculated with DFT-SCAN, as a function of μ_{Cu} under low Na (panel a, Cu_{1.94}Na_{0.06}ZnSnS₄) and high Na (panel b, Cu_{1.5}Na_{0.5}ZnSnS₄) doping conditions. These two dopant concentrations correspond to 3% and 25% Na-doping on the Cu sublattice, respectively, or 0.75 at.% and 6.25 at.% Na equivalently overall. Note that the at.% numbers used throughout are normalized per formula unit of Cu₂ZnSnS₄, which contains 25 at.% Cu, 12.5 at.% Zn and Sn, and 50 at.% S in its pristine state. Thus, replacing 25% of the Cu atoms within CZTS with Na atoms corresponds to an overall percentage of Na atoms in CZTS of 6.25 at.% (25% of 25 at.% Cu). Black lines in panel a reflect the ease of doping Na on a Cu-site (dashed line) or a Zn-site (dash-dot). Dotted vertical green lines in both panels signify the various Cu-environments considered (see Methods section), while the orange band $(\sim 0.22 - 0.25 \text{ eV})$ in each panel corresponds to the formation energies of disorder-inducing Cu_{Zn}+Zn_{Cu} antisites in pure CZTS.²³ Solid blue lines signify disorder-inducing antisites in Na-doped CZTS, including formation of Cu_{Zn}+Zn_{Cn} antisites near a doped Na atom (Na_{Cu}/Na_{Zn}) and disorder due to Naparticipation via Na_{Zn}+Zn_{Cu} (low Na) and Na_{Zn}+Zn_{Na} (high Na) antisites. Dashed pink lines in panel a reflect the formation of Cu-vacancies (V_{Cu}) adjacent to a doped Na site, while the solid red line indicates Zn-deficiency via Cu_{Zn} formation. The "(Sn)" and "(Zn)" text annotation accompanying each defect signifies that the Cu-site participating in the defect belong the Sn- and Zn-planes of the kesterite structure (Figure 1), respectively. For example, in the $Na_{Zn}+V_{Cu}$ (Sn) defect (dashed pink line in Figure 2a), the Cu-vacancy forms on a Cu-site in a Sn-plane adjacent to the Na_{Zn} antisite. Notably, we only include the lowest formation energies for defects with multiple possible configurations within the kesterite lattice. As an example, the Na_{Zn}+Zn_{Cu} defect involves two possible defect configurations, where Zn occupies an adjacent Cu site on the same Zn-plane or a neighboring Sn-plane. However,

Na_{Zn}+Zn_{Cu} (Sn) exhibits a higher formation energy (by ~0.03 eV) across all μ_{Cu} compared to Na_{Zn}+Zn_{Cu} (Zn), motivating us to include only the latter in Figure 2a. In the case of Na_{Cu} (Sn/Zn), formation energies of defects occurring on Sn- or Zn-planes differ marginally (<0.005 eV).

Under low Na-doping (Figure 2a), Na occupies Cu-sites under constrained Cu-poor to Cu-rich conditions, as indicated by the lower formation energy of $Na_{Cu}\ (Sn/Zn)\ (0.55{-}0.49$ eV, dashed black line) versus Na_{Zn} (~0.66-0.60 eV, dash-dot black line). Interestingly, under Cu-poor conditions, Na favors occupying Zn-sites (Na_{7n} \sim 0.41 eV) compared to Cu-sites (Na_{Cu} \sim 0.49 eV), qualitatively similar to the trends observed in low Ag-doped CZTS.²³ Notably, Maeda et al.⁵⁵ reported a higher formation energy for both $Na_{Cu}\ ({\sim}0.64\ eV)$ and Na_{Zn} (~0.51 eV) than our calculations under analogous Cu-poor conditions, presumably due to the use of the GGA XC functional in combination with experimental enthalpies instead of our purely theoretical estimate using SCAN. Cu-vacancies (dashed pink lines in Figure 2a), which form readily in undoped-CZTS²³ and have been predicted to reduce detrimental band gap fluctuations,²⁴ do not form readily under low Na-doping conditions, as indicated by the high formation energies of $Na_{Zn}+V_{Cu}$ (Sn) (~1.61-0.79 eV) and Na_{Cu} (Sn)+ V_{Cu} (Zn) (~1.29–0.66 eV). Additionally, Cu-poor conditions favor the formation of Zn-deficient CZTS under low Na-doping, signified by the reduction in formation energy of $Na_{Cu}+Cu_{Zn}$ (Zn) from ~0.56 eV at Cu-rich to ~0.31 eV at Cu-poor conditions (solid red line in Figure 2a).

Importantly, both low and high levels of Na-doping should effectively suppress formation of disorder-inducing antisites in kesterite, as indicated by the higher formation energies of all solid blue lines (in both panels of Figure 2) in contrast to pure CZTS (~0.22-0.25 eV, orange band). Specifically, $Na_{Zn}+Cu_{Zn}+Zn_{Cu}$ (Sn), $Na_{Cu}+Cu_{Zn}+Zn_{Cu}$ (Zn), and $Na_{Zn}+Zn_{Cu}$ (Zn) exhibit formation energies of ~0.75-0.5, 0.79-0.74, and 0.85-0.79 eV from Cu-rich to Cu-poor conditions (Figure 2a), respectively, while $Cu_{Zn}+Zn_{Cu}$ (Zn)



Figure 4. (a) Plots of the relative stabilities of the stannite and kesterite polymorphs and (b) display of the thermodynamic stabilities as quantified by the energy above the hull (E^{hull}) for various Na (blue bars) and Ca (orange bars) doping concentrations in kesterite Cu₂ZnSnS₄. Inset in (a) indicates the lowest energy stannite structure at 50% Na-doping. Doping percentage references the number of cation sites replaced by the dopant on the respective sublattice per formula unit of Cu₂ZnSnS₄.

and Na_{Zn}+Zn_{Na} display formation energies of ~1.19 and 1.08 eV across all Cu conditions (Figure 2b). Additionally, the formation energies of Na_{Cu}+Cu_{Zn}+Zn_{Cu} (Zn) defects do not change dramatically if the Cu_{Zn}+Zn_{Cu} complex forms one or two Sn-planes away from the Na_{Cu} antisite (~0.78–0.72 eV), signifying the efficient suppression of Cu_{Zn}+Zn_{Cu} formation via Na-doping.

Although the interaction energies of $Cu_{Zn}+Zn_{Cu}$ defect complexes adjacent to $Na_{Cu}~({\sim}0.24{-}0.25~eV)$ and Na_{Zn} (\sim 0.09 eV), calculated from the data in Figure 2a, are similar to or lower than the formation energy of Cu_{Zn}+Zn_{Cu} in undoped CZTS (0.22-0.25 eV), the interaction energy is not the relevant quantity of comparison. Doped CZTS samples are typically synthesized by preparing a doped precursor followed by high temperature annealing, where CZTS crystallizes into the kesterite structure.⁵⁶ The dopant is incorporated into the CZTS structure only when the kesterite structure forms during annealing, and formation of Cu_{Zn}+Zn_{Cu} complexes also occurs at that time. 24 Thus, as dopant incorporation and $\mathrm{Cu}_{\mathrm{Zn}}\mathrm{+Zn}_{\mathrm{Cu}}$ formation occur simultaneously, the formation energy of $Na_{Cu/Zn}+Cu_{Zn}+Zn_{Cu}$ is the relevant quantity to compare against the energy required to form Cu_{Zn} + Zn_{Cu} complexes in undoped CZTS.

The suppression of disorder-inducing antisites by Na, across doping concentrations and Cu conditions, is in contrast to the select doping and Cu conditions required by Ag and Cd to effectively suppress antisites,²³ highlighting that Na-doping may be an efficient means to improve performance of CZTS solar cells. Indeed, experimental studies have reported improved efficiencies of $Cu_2ZnSn(S,Se)_4$ cells with Na-doping,^{57–59} albeit with a focus on reducing carrier recombination at the CZTS–buffer layer interface rather than bulk Na incorporation.

Defects with Ca-Doping. Similar to Figure 2, the defect formation energies, calculated with DFT-SCAN, are plotted against μ_{Cu} under low Ca (panel a, Cu₂Zn_{0.94}Ca_{0.06}SnS₄) and high Ca (panel b, Cu₂Zn_{0.5}Ca_{0.5}SnS₄) doping conditions in Figure 3. These two dopant concentrations, respectively, correspond to 6% and 50% Ca-doping on the Zn sublattice or equivalently 0.75 at.% and 6.25 at.% Ca overall. Dash-dot and

dashed black lines in Figure 3a represent substituting Zn- and Cu-sites with Ca atoms, while solid blue lines in both panels of Figure 3 indicate disorder-inducing antisites. The dashed red line in panel a reflects formation of Cu-deficient CZTS via formation of $Ca_{Zn}+Zn_{Cu}$ antisites, with the Zn_{Cu} antisite occurring on the Sn-plane (as indicated by the "(Sn)" notation) of kesterite (Figure 1). Note that $Cu_2Zn_{0.5}Ca_{0.5}SnS_4$ prefers to form distinct Zn- and Ca-planes within kesterite (Figure 1). Hence, the $Cu_{Ca}+Ca_{Cu}$ (Ca) (Figure 3b) refers to the formation of a Ca_{Cu} antisite on a Ca-plane.

Unlike low Na-doping (Figure 2a), the high formation energies of both Ca_{Zn} and Ca_{Cu} (Zn) defects, ~1.13 eV and 2.26-2.45 eV, respectively (black lines in Figure 3a), suggest a high degree of difficulty in incorporating Ca into the kesterite structure under low doping conditions. Thus, the equilibrium doping concentration of Ca in the CZTS lattice should be significantly lower compared to Na (or Ag/Cd).²³ Notably, the kesterite structure can accommodate substantial doping concentrations of both Ag and Cd,^{23,28,29} which exhibit ionic radii of ~1.15 Å (1 Å) and 0.95 Å (0.78 Å), respectively, in octahedral (tetrahedral) coordination that are significantly larger than Cu⁺'s 0.77 Å (0.6 Å) and Zn²⁺'s 0.74 Å (0.6 Å) in octahedral (tetrahedral) coordination.³⁵ Thus, the similarity in tetrahedral ionic radii and oxidation states between Na⁺ (~1.02 Å in octahedral, 0.99 Å in tetrahedral) and Ag⁺ indicates comparable ease of doping.²³ Ca²⁺ (1.0 Å in octahedral) is sufficiently larger than Cd²⁺, so it displays a substantially higher formation energy for the isovalent Ca_{Zn} antisite (~1.13 eV) than the corresponding Cd_{Zn} (~0.12 eV^{23}). Note that the ionic radius of Ca²⁺ is similar to that of Na⁺ while being smaller than octahedral Ag⁺. Hence, the difficulty in isovalent Ca incorporation (Ca_{Zn}) , in contrast to Na (Na_{Cu}) , Ag (Ag_{Cu}) , and Cd (Cd_{Zn}) , is due to the combination of the higher oxidation state of Ca (2+ vs 1+ of Na and Ag) and its large ionic radius (especially vs Cd^{2+}). Analogously, the combined electrostatic and steric effects of a large divalent cation has been blamed for the lack of stable intercalation electrodes in beyond-Li energy storage systems.^{53,60–62}



Figure 5. Total density of states, calculated using GGA+U, are plotted for Na_2ZnSnS_4 (panels a and b) and Cu_2CaSnS_4 (panels c and d) compositions, adopting the kesterite (panels a and c) and stannite (panels b and d) polymorphs. Shaded blue (red) region signifies electronic up (down) spin states. Dashed black lines indicate the valence and conduction band edges. The energy scale is set to zero at the valence band maximum (VBM). Number (in eV) within each panel corresponds to the band gap for the given structure and composition.

Nevertheless, if Ca is able to be incorporated, it should be quite effective in suppressing disorder-inducing antisites under both low and high doping conditions and across μ_{Cu} in comparison to undoped CZTS (~0.22-0.25 eV for Cu_{Zn} + Zn_{Cu} formation, orange bands in Figure 3). For example, $Ca_{Cu}+Cu_{Zn}$ (Zn), $Ca_{Zn}+Cu_{Zn}+Zn_{Cu}$ (Zn), and $Ca_{Cu}+Cu_{Zn}+Zn_{Cu}$ (Zn) antisites exhibit large formation energies of ~1.33, 1.36, and 2.37-2.56 eV, respectively, under low Ca-doping (solid blue lines in Figure 3a). Similarly, under high Ca-doping (Figure 3b), Cu_{Ca}+Ca_{Cu} (Sn) and $Cu_{Ca}+Ca_{Cu}$ (Ca) display formation energies of 1.33 and 1.44 eV, respectively. Additionally, any Ca incorporation may penalize defects that induce Cu-deficiency, particularly under Cu-poor conditions, as indicated by the increase in formation energy of Ca_{Zn}+Zn_{Cu} (Sn) from ~2.24 eV at Cu-rich to 2.43 eV at Cu-poor (dashed red line in Figure 3a). Thus, Ca would efficiently suppress disorder-inducing antisite formation within the kesterite via steric interactions, if it could be doped successfully into the structure.

Stability. Panel a of Figure 4 plots the relative stability of the stannite and kesterite polymorphs, $E_{\text{stannite}} - E_{\text{kesterite}} = \Delta E$, under different doping concentrations for Na (blue bars) and Ca (orange). These doping percentages of 25, 50, 75, and

100% in CZTS, respectively, refer to Na compositions of Cu1.5Na0.5ZnSnS4, CuNaZnSnS4, Cu0.5Na1.5ZnSnS4, and Na₂ZnSnS₄, respectively, containing 6.25, 12.5, 18.75, and 25 at.% Na. Likewise, Ca-doping percentages of 25, 50, 75, and 100% in CZTS, respectively, refer to compositions of $Cu_2Zn_{0.75}Ca_{0.25}SnS_4,\ Cu_2Zn_{0.5}Ca_{0.5}SnS_4,\ Cu_2Zn_{0.25}Ca_{0.75}SnS_4,$ and Cu₂CaSnS₄, respectively, containing 3.125, 6.25, 9.375, and 12.5 at.% Ca. Positive (negative) values of ΔE correspond to increasing kesterite (stannite) stability. Without any dopant, kesterite is more stable than the stannite structure by ~ 0.028 eV/f.u., in agreement with previous theoretical estimates.^{23,25,63} Interestingly, increasing Na-concentration within the CZTS lattice exhibits a strong nonmonotonic trend in the relative stability of the polymorphs. For example, as the Nacontent increases from 0% to 50%, the stannite structure becomes increasingly stable as indicated by $\Delta E = 0.008$ and -0.1 eV/f.u., respectively. The inset within Figure 4a indicates the lowest energy atomic arrangement among possible Na-Cu orderings within the stannite unit cell (red, blue, gray, green, and yellow spheres represent Na, Cu, Zn, Sn, and S, respectively). At high Na-concentrations, kesterite becomes more stable, signified by $\Delta E = \sim 0.14$ and ~ 0.34 eV/f.u. at 75% and 100% Na, respectively. Thus, either low (<25%) or high $(\geq 75\%)$ concentrations of Na will stabilize the kesterite polymorph. In the case of Ca, there is no variation in the stability of the kesterite up to ~50% Ca, while at 100% Ca, stannite becomes more stable by ~0.18 eV/f.u., qualitatively similar to the trends observed upon Cd-doping in CZTS.²³

The thermodynamic stability, as quantified by E^{hull} (see Methods section), indicates whether a given composition is stable against decomposition into other secondary phases. Hence, we calculated the E^{hull} at various Na (blue bars) and Ca (orange) doping concentrations within CZTS, as displayed in Figure 4b. A stable phase is generally synthesizable and is likely to function long-term as a reliable PV. For example, undoped- Cu_2ZnSnS_4 and kesterite-Na₂ZnSnS₄ exhibit $E^{hull} = 0$ (Figure 4b), signifying that the corresponding kesterite phases are thermodynamically stable, should be synthesizeable, ⁶⁴⁻⁶⁶ and should not display any decomposition under reasonable synthesis or operating conditions. Interestingly, none of the intermediate Na-doped CZTS compositions are thermodynamically stable, with $Cu_{1.5}Na_{0.5}ZnSnS_4$, $CuNaZnSnS_4$, and $Cu_{0.5}Na_{1.5}ZnSnS_4$ displaying $E^{hull} = 0.24$, 0.28, and 0.27 eV/ f.u., respectively. Thus, intermediate doping of Na into CZTS will lead to phase separation, forming Cu₂ZnSnS₄ and Na₂ZnSnS₄ domains. Doping small concentrations of Na (on the order of $x_{Na} \sim 0.015$, Figure 2a) into CZTS should be possible based on the reasonable formation energy of Na_{Cu} (~0.49–0.55 eV) and Na $_{\rm Zn}$ (~0.41–0.66 eV) defects within the kesterite structure. Cu2CaSnS4 is thermodynamically unstable ($E^{\text{hull}} \sim 0.66 \text{ eV/f.u.}$) and will decompose into Cu₂SnS₃ and CaS₂ in agreement with the high formation energies (>1 eV) of Ca_{Zn} and Ca_{Cu} defects under low Cadoping (black lines in Figure 3a). Analogously, $Cu_2Ca_{0.5}Zn_{0.5}SnS_4$ ($E^{hull} \sim 0.48 \text{ eV/f.u.}$) will decompose into Cu₂ZnSnS₄, Cu₂SnS₃, and CaS. The thermodynamic instability of CZTS at high Ca content can be attributed to the combined effect of a large ion with a higher oxidation state (see discussion after Figure 3). Thus, doping significant amounts of Ca within the CZTS lattice may not be feasible and will likely lead to the formation of decomposition products.

Band Gaps. Aside from considering the ease of doping and the formation of disorder-inducing antisites (Figures 2 and 3), the relative stability of the kesterite and stannite polymorphs (Figure 4a), and the overall thermodynamic stability (Figure 4b) of Na- and Ca-doped CZTS, it is important to understand the impact of Na and Ca incorporation on electronic properties, specifically the band gap in doped-CZTS. Thus, we calculated the total density of states (DOS) of both the kesterite (panels a and c) and the stannite (panels b and d) polymorphs of NZTS (panels a and b) and Cu₂CaSnS₄ (CCTS, panels c and d) compositions, using the GGA+Ufunctional, as displayed in Figure 5. Although GGA+U does not provide quantitatively accurate band gaps that are comparable to photoemission/inverse photoemission (PES/ IPES) measurements,^{67,68} the qualitative trends are often reliable. Previous GGA+U calculations reported band gaps of \sim 0.96 and \sim 0.79 eV in the kesterite and stannite structures of undoped CZTS, respectively.²³

Any Ca-doping within CZTS should cause a negligible increase in band gap within the kesterite structure (\sim 1.0 eV in CCTS, Figure 5c vs 0.96 eV in CZTS), while a nontrivial increase should be observed within the stannite structure (\sim 1.27 eV in CCTS, Figure 5d vs 0.79 eV in CZTS). Given the relative stability of kesterite (vs stannite) under low Cadoping (<50% in Figure 4a), Ca incorporation, if any, should

have a marginal impact on the electronic properties of CZTS. Na-doping in CZTS should result in a large band gap increase, as indicated by the substantially higher band gaps of \sim 2.14 and \sim 1.45 eV in kesterite- and stannite-NZTS (Figure 5a,b), respectively, compared to undoped CZTS. Indeed, absorption measurements reveal an optical band gap of ~ 3.1 eV in NZTS,⁶⁶ about twice as high as the 1.4–1.6 eV in pure CZTS.⁶ Also, ultraviolet-visible (UV-vis) absorption spectra⁵⁶ exhibit a small increase in the onset of absorption, from 1.5 eV at 0% Na to 1.6 eV at 2% Na-doping, qualitatively consistent with our calculations at full Na-doping. Interestingly, the predicted increase in band gap from CZTS to NZTS is larger within the kesterite structure (~1.18 eV larger) versus the stannite (~0.66 eV larger), unlike with Ca. Hence, high levels of Nadoping may detrimentally affect the performance of CZTS solar cells via formation of NZTS domains (Figure 4b) that exhibit nonoptimal PV band gaps. Further, combining the electronic properties with the efficient suppression of disorderinducing antisites (Figure 2a) and the stability of the kesterite at low Na-doping (<25%, Figure 4), low levels of Na incorporation within kesterite CZTS provides a promising pathway to improve the efficiency of CZTS solar cells without sacrificing its optimal band gap.

CONCLUSIONS

CZTS-based solar cells, which could form a crucial component of sustainable, beyond-Si thin-film technologies, often suffer from poor efficiencies, attributed to the formation of Cu_{Zn} +Zn_{Cn} antisites that induce disorder within the kesterite structure (Figure 1). A pathway to mitigate the formation of such antisites is to dope the CZTS structure with large isovalent dopants, such as Na⁺ for Cu⁺ and Ca²⁺ for Zn²⁺ that penalize the antisites due to steric interactions. Indeed, previous experimental and theoretical studies have demonstrated improvements in V_{oc} and efficiency of CZTS cells doped with Ag and Cd. Hence, we explored the role of Na and Ca as potential isovalent dopants in CZTS by calculating defect formation energies, thermodynamic stabilities, and electronic structure properties, using DFT-based calculations. Specifically, we used the SCAN functional to calculate the defect and thermodynamic properties while employing GGA +U+D to qualitatively estimate band gap variations with doping.

On the basis of the formation energies of Na_{Cu} and Na_{Zn} defects (~0.41-0.66 eV, Figure 2a), we report that Na-doping within the kesterite structure is feasible, while the high formation energy of Ca_{Cu} and Ca_{Zn} antisites (>1 eV, Figure 3a) hinders Ca incorporation. However, if incorporated, both Na and Ca are effective in mitigating the formation of disorderinducing antisites, across doping and Cu-chemical-potential conditions, as indicated by the higher formation energies of such antisites in doped CZTS versus pristine CZTS (Figures 2 and 3). Our results on the relative stabilities of the kesterite and stannite polymorphs and the overall thermodynamic stabilities of various doped compositions (Figure 4) signify that the addition of large amounts of Na into CZTS would cause a phase separation, resulting in domains of CZTS and NZTS. High concentrations of Ca are thermodynamically unstable and will lead to spontaneous decomposition, forming secondary products such as Cu₂SnS₃ and CaS. Additionally, band gaps in NZTS and CCTS (Figure 5) are higher than CZTS for both the kesterite and stannite polymorphs, with the impact of Na on increasing the band gap in kesterite

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significantly larger than Ca. Thus, doping high concentrations of Na may result in a large increase in band gap, away from the optimal range for PV applications. Finally, integrating defect, thermodynamic, and electronic properties of Na/Ca-doped CZTS, we identify doping low concentrations of Na in kesterite CZTS to be a potential route to improve the photovoltaic performance of CZTS-based solar cells.

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Notes

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