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Extended anti-site defects in tetrahedrally bonded semiconductors

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Typically point defects are modeled by adding, removing, or exchanging at most few atoms around a given lattice site. We demonstrate the possibility of formation of extended anti-site defects that involve complex, non-local atomic rearrangements, which cannot be captured within a simple point defect model. We illustrate formation of extended anti-site defects in Cu_2SnS_3 and Cu_2SnZnS_4 solar absorbers where they lower the formation energy by up to about 1 eV per defect. These extended anti-site configurations can dramatically change the stoichiometries and doping properties of multinary semiconductors that have a propensity towards disorder.

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Point defects in crystalline materials are ubiquities forming either as a result of the thermodynamic defect equilibrium¹ or due to non-equilibrium processes during crystal growth or deposition². In semiconductors, point defects largely control the electrical conductivity and strongly influence optical properties³. Their formation is therefore of particular importance to operation of large number of optoelectronic devices⁴ and pn-junction photovoltaic (PV) cells are an important example.

The design of materials for PV and other optoelectronic applications requires thorough understanding of the materials defect chemistry. First principles supercell calculations provide invaluable insight into the formation and properties of defects and dopants, and are now a mainstay of computational materials science⁵. Calculations of the formation energies and the thermal and optical transition levels of defects are used to assess the potential of solar absorber materials $^{6-9}$, to predict carrier densities, e.g., in transparent conducting oxides $^{10-12}$, and to identify recombination $centers^{13}$. Since the first supercell calculations^{14,15} of defect formation energies, the methodology for first principles defect theory has been constantly refined, for example addressing image charge corrections^{16,17}, the DFT band gap problem¹⁸⁻²⁰ defect pairing and clustering 12,21 , as well as vibrational effects^{22,23}. However, such supercell defect calculations are generally limited to point defects where either a single or a small number of atoms are added, removed or exchanged around a given lattice site.

Here we identify new type of carrier generating defect—extended anti-site defect—that can form in materials with a tendency to disorder. In contrast to a conventional point defect model, formation of an extended anti-site defect involves complex and non-local rearrangements and therefore cannot be captured by simple atomic rearrangements around a single lattice site. We illustrate this mechanism in tetrahedrally bonded multinary solar absorbers Cu_2SnS_3 (CTS) and Cu_2SnZnS_4 (CZTS), where extended Cu_{Sn} anti-site defects have ≈ 1 eV lower formation energy compared to the corresponding crystal-lographic point defects in the ordered structure.

The structures of CTS and CZTS can be derived by appropriate ordering of Cu, Zn, Sn atoms on the cation sites of the ZnS zincblende lattice⁹. The local ordering of cations around sulfur lattice site in these compounds is strongly constraint due to so-called octet rule which states that anions prefer cation coordinations leading to eight electrons in anions' valence shell. As a result, the ground state structures of CTS and CZTS are built from S based tetrahedral motifs that offer the smallest deviation from the fully occupied sulfur valence shell (the number of electrons in the sulfur valence shell is $N_v = 8$): the tetragonal kesterite CZTS (sg, $I\bar{4}$) structure is built from S-Cu₂SnZn motif ($N_v = 8$) whereas the monoclinic CTS (sg, Cc) structure is built from S-Cu₃Sn ($N_v = 7.75$) and S-Cu₂Sn₂ ($N_v = 8.5$) motifs^{24,25}.

The formation of cation anti-site defects necessarilv changes local sulfur environment. To quantify the energetics of such changes we employ a model Hamiltonian that expands the formation energy in terms of S-Cu_iSn_jZn_{4-i-j} tetrahedral motifs: $\Delta_f E =$ $2\sum_{(i,j)} n(i,j)e(i,j)$, where n(i,j) count the number of S-Cu_iSn_iZn_{4-i-j} motifs and e(i, j) are the expansion parameters (Tab. I). The parameters of the model Hamiltonian were fitted to DFT+U calculated formation energies CZTS and CTS with random cation configurations²⁶. Note that within the model Hamiltonian, the energy depends only on the relative fractions of the S-centered motifs, but not on their arrangement. Despite this simplification, this model captures the essential energetics in disordered CTS and $CZTS^{26}$.

In the following, we are employing the model Hamiltonian for Monte-Carlo sampling, but then also perform

TABLE I: Parameters of the motif-based model Hamiltonian in ${\rm eV}/{\rm atom}.$

S-Cu ₄	S-Cu ₃ Sn	$S-Cu_2Sn_2$	$S-CuSn_3$	S-Sn ₄
-0.238	-0.492	-0.463	-0.254	-0.026
$S-Cu_3Zn$	$S-Cu_2SnZn$	$S-CuSnZn_2$	S-CuZn ₃	S-Zn ₄
-0.404	-0.663	-0.790	-0.914	-1.083
$S-Cu_2Zn_2$	$S-CuSn_2Zn$	$S-Sn_3Zn$	$S-Sn_2Zn_2$	S-SnZn ₃
-0.679	-0.563	-0.379	-0.565	-0.880



FIG. 1: First and second coordination shell of (a) Sn atom and (b) Cu_{Sn} anti-site defect in monoclinic Cu_2SnS_3 . S-based tetrahedra: S- Cu_2Sn_2 (yellow), S- Cu_3Sn (blue), S- Cu_4 (red).

DFT+U calculations on the resulting structures. Only charge neutral supercells are considered in the present work. It should be noted, however, that the disordered structures can implicitly contain mutually compensating defects pairs, such as, e.g., the Zn_{Cu}^+ - Cu_{Zn}^- pair in CZTS. The DFT+U calculations are performed using the VASP code²⁷, the Perdew-Burke-Ernzerhof exchangecorrelation functional²⁸ and U=5eV for the Cu-d shell²⁹. For the Cu_{Sn} defect formation energy we used the elemental chemical potentials of Ref.³⁰.

Let us first analyze formation of Cu_{Sn} anti-site defect in cation ordered monoclinic CTS. The Sn site in CTS is coordinated by 4 S atoms in the first coordination shell and by 2 Sn and 10 Cu atoms in the second coordination shell which together form 2 S-Cu₃Sn and 2 S-Cu₂Sn₂ motifs (Fig. 1). By replacing the central Sn atom with Cu atom, these motifs are converted to two S-Cu₄ motifs and two S-Cu₃Sn motifs, respectively. The S-Cu₄ sulfur coordination is a high energy S environment as it violates the octet rule by 1 electron ($N_v = 7$), which raises the question: Is it geometrically possible to form the Cu_{Sn} anti-site defect without the formation of high-energy S-Cu₄ motifs?

According to the model Hamiltonian, the removal of S-Cu₄ motifs in the reaction S-Cu₄ + S-Cu₂Sn₂ \rightarrow 2 S-Cu₃Sn is exothermic by -0.57 eV. In fact, from point of view of the composition, the stoichiometry change due to a Cu_{Sn} anti-site defect could be accommodated by converting S-Cu₂Sn₂ motifs into S-Cu₃Sn motifs, resulting in a formation energy that is 1.14 eV lower compared to the crystallographic point defect that creates two high-energy S-Cu₄ motifs. Whether or not such low energy defects are possible is, however, not immediately obvious as in the ordered monoclinic CTS there are no Sn sites surrounded by only S-Cu₂Sn₂ motifs. Consequently, the formation of such low energy Cu_{Sn} anti-site defects must require more complex cationic rearrangements.

In order to check the possibility of the formation of such low energy Cu_{Sn} defects configurations, we first consider all possible defect complexes that include atomic rearrangements up to the second coordination shell of the Cu_{Sn} defect site. There are $\binom{12}{2} = 66$ possible arrangements of Cu and Sn atoms in the second shell. Each configuration can be thought of as a complex defect (1



FIG. 2: Formation of Cu_{Sn} in CTS: The smallest number of high-energy motifs after completion of simulated annealing with the motif-based model Hamiltonian as a function of the supercell size.

+ k) Cu_{Sn} + k Sn_{Cu} , where $k \in \{0, 1, 2\}$. Interestingly, however, none of these complex defects avoids formation of high-energy motifs such as S-Cu₄.

The number of possible Cu and Sn configurations explodes, as further coordination shells are included. To efficiently search for possible Cu_{Sn} defects that avoid formation of high-energy S-Cu₄ motifs, we perform simulated annealing optimization with Metropolis Monte Carlo method and the motif-based model Hamiltonian²⁶. First, we create a single Cu_{Sn} anti-site defect and randomize cation configuration in the supercell, then the system is equilibrated at 1773 K and finally annealed to 0 K. For each unit cell size we perform 15 randomly initialized runs.

Figure 2 shows the smallest number of high energy motifs after completion of the simulated annealing as a function of the cell size: the solid line shows the number of the S-Cu₄ motifs whereas the dashed line shows the total number of the non-ground state motifs (motifs of S-Cu₄, S-CuSn₃, and S-Sn₄). The annealing removes the S-Cu₄ motifs, and in cell sizes larger than 144 atoms, the Cu_{Sn} anti-site defects can form without creating nonground state motifs. In cell sizes of 180 and 300 atoms, however, S-Sn₄ motifs form as the reaction 2 S-Cu₄ + 5 S-Cu₂Sn₂ \rightarrow S-Sn₄ + 6 S-Cu₃Sn is downhill in energy ($\Delta E = -0.43 \text{ eV}$). Thus even in cell sizes of 300 atoms periodic boundary conditions affect the types of motifs that are formed together with Cu_{Sn} anti-site defect.

Clearly, complete elimination of high energy motifs requires *non-local* atomic rearrangement that can only be captured in large supercells with appropriate periodic boundary conditions which for Cu_{Sn} are satisfied in 144, 240 and 432 atom cells but not in 300, 180 and smaller than 144 atom cells. Such complex rearrangements cannot be described within a simple point defect or cluster of point defects model. In fact, after creating the



FIG. 3: Formation energy of Cu_{Sn} anti-site defects calculated with DFT+U as a function of the number of S-Cu₄ motifs. The formation energy is evaluated using disordered supercell of CTS as reference host cell and reference chemical potentials of elemental phases in the chemical standard state ($\Delta \mu_{Cu} = \Delta \mu_{Sn} = 0$).

crystallographic point defect Cu_{Sn} in the ordered monoclinic structure of CTS and minimizing the (free) energy during the Monte Carlo simulations, the resulting cation arrangement is highly disordered (cf. bottom panel in Fig. 4).

Figure 3 shows the formation energy of Cu_{Sn} anti-site defects calculated with DFT+U for 26 cells of 144 atoms with different numbers of S-Cu₄ motifs generated during simulated annealing. The formation energy is evaluated using a stoichiometric, but disordered supercell of CTS as reference host cell and reference chemical potentials of elemental phases in the chemical standard state $(\Delta \mu_{\rm Cu} = \Delta \mu_{\rm Sn} = 0)$. The formation energy of Cu_{Sn} is approximately proportional to the number of S-Cu₄ motifs with a slope of 0.67 eV showing that this highenergy motif dominates the magnitude of the formation energy. Both the value of the slope and linearity of the formation energy is in good agreement with the motifbased model Hamiltonian predicting that elimination of a single S-Cu₄ motif lowers the energy by -0.57 eV. The Cu_{Sn} anti-site defect formed without any S-Cu₄ motifs has on average 1.34 eV lower formation energy compared to the Cu_{Sn} point defect in the ordered CTS lattice which creates two S-Cu4 motifs in the absence of disorder (cf. Fig. 1).

The large energy reduction due to the removal of the high energy motifs leads to an essentially zero formation energy of Cu_{Sn} in disordered CTS. From a different perspective, taking the ordered ground state structure of CTS as reference cell, the formation energy of the extended anti-site becomes cell size dependent, because it necessitates cation disorder (in Ref.²⁶, we determined an energy difference of 9 meV/atom between ordered and disordered CTS). For a 144 cell with a single Cu_{Sn} defect, the energy gain due to removal of high-energy motifs



FIG. 4: Top: Mixing energies between CTS and Cu_3SnS_4 as a function of alloy compositions composition x, $Cu_{8+x}Sn_{4-x}S_{12}$. Bottom: Distribution of S-Cu₂Sn₂ (yellow) and S-Cu₄ (red) motif centers in 144 atom cells with two Cu_{Sn} anti-site defects, for clarity S-Cu₃Sn are removed.

is approximately offset by the energy cost due to the ensuing disorder. However, the extended anti-site is still strongly favored over the crystallographic point defect due to the higher entropy associated with the cation disorder. Further, once the energy cost associated with disorder is overcome, a larger number of extended Cu_{Sn} defects can be accommodated within the same cell volume without formation of high-energy motifs. Consequently, the formation energy of disordered CTS becomes lower that that of ordered CTS above a certain concentration of Cu_{Sn} defects. This is seen in Fig. 4, showing the mixing enthalpy $\Delta_m H$ as a function of the composition x in the $Cu_{8+x}Sn_{4-x}S_{12}$ alloy. The energy of ordered CTS with Cu_{Sn} point defects rises very steeply with increasing deviation from the CTS stoichiometry and above x > 0.06exceeds that of the disordered alloy resulting from formation of extended anti-site defects. These computational predictions are also supported by recent experimental evidence of a strong correlation between atomic ordering and the hole carrier density which is a sensitive indicator of off-stoichiometry 31 .

A similar energy lowering due to complex atomic rearrangements also occurs for the opposite anti-site defect Sn_{Cu} in CTS. Substitution of Cu by Sn in CTS converts 3 S-Cu₃Sn and S-Cu₂Sn₂ motifs into 3 S-Cu₂Sn₂ and S-CuSn₃ motifs. The latter sulfur environment violates the octet rule by 1.25 electrons and can be eliminated via

 $S-CuSn_3 + S-Cu_3Sn \rightarrow 2 S-Cu_2Sn_2$, a pathway that is exothermic by -0.36 eV.

The formation of low-energy extended anti-site defects is not limited to CTS and should also occur in other multinary tetrahedrally bonded materials. A technologically important example is CZTS which has attracted high interest as a solar absorber material^{32,33}. The formation of Cu_{Sn} anti-site point defect in this material leads to the creation of four unfavorable S-Cu₃Zn motifs, which violate the octet rule by 0.75 electrons. The pathway for the removal of the S-Cu₃Zn motifs is more complex, S-Cu₃Zn + 4 S-Cu₂SnZn \rightarrow S-CuSnZn₂ + S- $CuZn_3 + 3$ S- Cu_3Sn ($\Delta E = -0.24$ eV) and leads to total energy lowering by 0.96 eV. Note that formation of the notorious Cu_{Zn} and Zn_{Cu} anti-site defects^{34–36} leads to relatively stable S-Cu₃Sn and S-CuSnZn₂ motifs and energy minimization in the disordered CZTS lattice does not lower their formation energy.

We now turn to discuss the broader implications of the present model for extended anti-site defects. As illustrated by the case of CTS, the failure to include these complex non-local atomic rearrangements can lead to qualitatively wrong conclusions. Specifically, we found that within the conventional point defect model, Cu vacancies are the dominant p-type defect, which would imply that the observed hole concentrations in the range between $10^{17} - 10^{21}$ cm³ come along with Cu-deficiency^{31,37}. However, the steep increase of p-type doping at high [Cu]/([Cu]+[Sn]) ratios was clearly inconsistent with the point defect model. The large reduction of the Cu_{Sn} formation energy due to the effect of disorder reconciles this compositional trend. The extended anti-site defect differs from the substitutional Cu_{Sn} defect also in its electronic behavior. Due to the large valence mismatch between Cu(I) and Sn(IV), the Cu_{Sn} point defect is a highly charged triple acceptor, with a deep and localized acceptor state³⁷. In contrast, in the disordered configuration as an extended anti-site defect, there is no clearly defined site of the dopant, the hole charge is delocalized, and the acceptor state is energetically close to the valence band continuum. It should further be noted that the complex atomic structure of the extended anti-site defects complicates the thermodynamical modeling of the defect and carrier concentrations, which generally rely on the configurational entropy of defects on a lattice¹. Such predictions could be accomplished via grand-canonical Monte-Carlo simulations, which, however, lie beyond the scope of the present work.

For CZTS, there exists a body of literature on defect formation energies, e.g.^{38–40}. The earlier works^{38,39} found a formation energy of the Cu_{Sn} defect of about 1.1 eV ($\Delta \mu_{Cu} = \Delta \mu_{Sn} = 0$). However, due to deficiencies of the standard PBE functional, these calculations also predicted unphysical negative formation energies for the Cu_{Zn} acceptor. This issue was clarified and corrected by a later hybrid functional study⁴⁰, in which the Cu_{Sn} formation energy was found at 2.4 eV ($\Delta \mu_{Cu} = \Delta \mu_{Sn} = 0$). Our GGA+U calculated value of 2.1 eV is close to this



FIG. 5: Mixing energy for (a) CTS–Cu₃SnS₄–ZnS and (b) CTS–CZTS–Cu₃SnS₄ systems calculated withing the motifbased model Hamiltonian.

hybrid functional result. Since the Cu_{Sn} formation energy is reduced by up to 1.2 eV depending on the actual growth conditions⁴⁰, the additional reduction of about 1 eV due to the non local atomic rearrangement will render Cu_{Sn} at least as important as the acceptor defects Cu_{Zn} and V_{Cu} . A further implication is that a high Cu composition can considerably increase the p-type doping, but at the same time causes disorder that can cause harmful potential fluctuations or even trap states^{26,41,42}.

An important consequence of a significant decrease in the formation energy of anti-site defects in CTS and CZTS is the increased ability of these materials to sustain high degree off-stoichiometry without phase separation. For instance, the formation of Cu_{Sn} defects in Cu_2SnS_3 can be viewed as admixing of Cu_3SnS_4 , i.e., the formation of a $Cu_{8+x}Sn_{4-x}S_{12}$ alloys within a structurally coherent tetrahedrally bonded phase. Note that for point defect substitution, the initial slope of the mixing enthalpy at x = 0 equals the defect formation energy of the Cu_{Sn} defect. Hence, the lowering of the defect formation energy due to the disorder correspondingly reduces the mixing enthalpy (cf. Fig. 4).

The energy minimization via non-local rearrangements can be extended to the wider CTS-Cu₃SnS₄-ZnS composition space, which includes CZTS. Figure 5(a) shows the mixing energy calculated within the model Hamiltonian for 768 atom cells. We observe positive mixing enthalpies along the Cu₃SnS₄-ZnS line, suggesting phase separation, but negative enthalpies along the CTS-ZnS line, due to the formation of the stable quaternary CZTS compound.

The mixing enthalpies for the compositional space bounded by CTS-Cu₃SnS₄-CZTS, shown in Fig. 5(b), are strictly zero within the model Hamiltonian. This is because the energetically unfavorable motifs such as S-Cu₄ or S-Cu₃Zn are eliminated during the Monte-Carlo simulation, and the resulting disordered structures are composed only of the native motifs of the constituents CZTS, Cu₃SnS₄, and CTS in respective proportions. While the zero mixing enthalpies would suggest continuous solid solutions, we note that a certain energy gain due to long range ordering in case of the stoichiometric end compounds is not captured by the model Hamiltonian. Thus, complete mixing is usually not attained in reality. Nevertheless, the extended defect model accounts for the fact that CZTS tolerates a high degree of off-stoichiometry along with maintaining a high level of disorder, rarely fully developing the cation ordering of the kesterite structure^{34,35,37}.

In conclusion, we have shown that complex, non-local atomic rearrangements can dramatically alter the defect physics in multinary tetrahedrally bonded materials. The formation of such extended anti-site defects is promoted by a large enthalpy gain due to removal of high energy motifs and a small enthalpy cost for disorder. Extended Cu_{Sn} anti-site defects in CTS and CZTS are remarkable examples as the energy lowering is in the order of 1 eV per defect. Such a large change may significantly affect defect chemistry and the electrical doping of the material. The extended anti-site defects can also considerably widen the compositional stability range of

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- ¹ F. A. Kröger and H. J. Vink, **3**, 307 (1956).
- ² H. Zeng, G. Duan, Y. Li, S. Yang, X. Xu, and W. Cai, Advanced Functional Materials **20**, 561 (2010).
- ³ F. Agulló-López, C. R. A. Catlow, and P. D. Townsend, *Point defects in materials*, vol. 149 (Academic Press London, 1988).
- ⁴ S. M. Sze and K. K. Ng, *Physics of semiconductor devices* (John Wiley & Sons, 2006).
- ⁵ C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti, and C. G. Van de Walle, Rev. Mod. Phys. 86, 253 (2014).
- ⁶ P. Zawadzki, L. L. Baranowski, H. Peng, E. S. Toberer, D. S. Ginley, W. Tumas, S. Lany, and A. Zakutayev, Appl. Phys. Lett. **103**, 253902 (2013).
- ⁷ S. Demers and A. van de Walle, Phys. Rev. B 85, 195208 (2012).
- ⁸ R. Sun, M. K. Y. Chan, S. Y. Kang, and G. Ceder, Phys. Rev. B 84, 035212 (2011).
- ⁹ S. Chen, X. G. Gong, A. Walsh, and S.-h. Wei, Phys. Rev. B **79**, 165211 (2009).
- ¹⁰ T. Zacherle, P. C. Schmidt, and M. Martin, Phys. Rev. B 87, 235206 (2013).
- ¹¹ P. Ágoston, C. Körber, A. Klein, M. J. Puska, R. M. Nieminen, and K. Albe, Journal of Applied Physics **108**, 053511 (2010).
- ¹² A. Zakutayev, N. H. Perry, T. O. Mason, D. S. Ginley, and S. Lany, Applied Physics Letters **103**, 232106 (2013).
- ¹³ S. Lany and A. Zunger, Physical Review Letters **100**, 016401 (2008).
- ¹⁴ J. E. Northrup and S. B. Zhang, Phys. Rev. B **47**, 6791 (1993).
- ¹⁵ S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991).
- ¹⁶ C. Freysoldt, J. Neugebauer, and C. G. Van de Walle, Phys. Rev. Lett. **102**, 016402 (2009).
- ¹⁷ S. Lany and A. Zunger, Phys. Rev. B **78**, 235104 (2008).
- ¹⁸ F. Oba, A. Togo, I. Tanaka, J. Paier, and G. Kresse, Phys. Rev. B **77**, 245202 (2008).
- ¹⁹ P. Rinke, A. Janotti, M. Scheffler, and C. G. Van de Walle, Phys. Rev. Lett. **102**, 026402 (2009).

the parental structure (e.g., the underlying zinc-blende lattice of CTS and CZTS), but at the same time break the long range ordering on the cation sub-lattice, causing disorder with potential impact on the electronic properties. Finally, we note that the mechanism of extended anti-site defect formation is a rather general possibility in multinary materials with a tendency to disorder.

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- ²⁰ H. Peng, D. O. Scanlon, V. Stevanovic, J. Vidal, G. W. Watson, and S. Lany, Phys. Rev. B 88, 115201 (2013).
- ²¹ S. B. Zhang, S.-H. Wei, A. Zunger, and H. Katayama-Yoshida, Phys. Rev. B **57**, 9642 (1998).
- ²² A. Alkauskas, J. L. Lyons, D. Steiauf, and C. G. Van de Walle, Phys. Rev. Lett. **109**, 267401 (2012).
- ²³ V. Kosyak, N. B. Mortazavi Amiri, A. V. Postnikov, and M. A. Scarpulla, Journal of Applied Physics **114**, 124501 (2013).
- ²⁴ Y. T. Zhai, S. Chen, J. H. Yang, H. J. Xiang, X. G. Gong, A. Walsh, J. Kang, and S. H. Wei, Phys. Rev. B 84, 075213 (2011).
- ²⁵ S. Delbos, EPJ Photovoltaics **3**, 35004 (2012).
- ²⁶ P. Zawadzki, A. Zakutayev, and S. Lany, Phys. Rev. Applied **3**, 034007 (2015).
- ²⁷ G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
- ²⁸ J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **78**, 1396 (1997).
- ²⁹ S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).
- ³⁰ V. Stevanović, S. Lany, X. Zhang, and A. Zunger, Phys. Rev. B 85, 115104 (2012).
- ³¹ L. L. Baranowski, K. McLaughlin, P. Zawadzki, S. Lany, A. Norman, H. Hempel, R. Eichberger, T. Unold, E. S. Toberer, and A. Zakutayev, Phys. Rev. Appl. p. (accepted) (2015).
- 32 S. Siebentritt, Thin Solid Films **535**, 1 (2013).
- ³³ W. Wang, M. T. Winkler, O. Gunawan, T. Gokmen, T. K. Todorov, Y. Zhu, and D. B. Mitzi, Advanced Energy Materials 4, 1301465 (2014).
- ³⁴ J. J. S. Scragg, L. Choubrac, A. Lafond, T. Ericson, and C. Platzer-Björkman, Applied Physics Letters **104**, 041911 (2014).
- ³⁵ S. Schorr, Solar Energy Materials and Solar Cells **95**, 1482 (2011).
- ³⁶ S. Chen, J.-H. Yang, X. G. Gong, A. Walsh, and S.-H. Wei, Physical Review B 81, 245204 (2010).
- ³⁷ L. Baranowski, P. P. Zawadzki, S. T. Christensen, D. Nordlund, S. Lany, A. C. Tamboli, L. Gedvilas, D. S. Ginley,

W. Tumas, E. S. Toberer, et al., Chem. Mater. 26, 4951 (2014).

- 38 A. Nagoya, R. Asahi, R. Wahl, and G. Kresse, Phys. Rev.
- ^A Nagoya, R. Asam, R. Wain, and G. Hiesse, Phys. Rev. B 81, 113202 (2010).
 ^S S. Chen, J.-H. Yang, X. G. Gong, A. Walsh, and S.-H. Wei, Phys. Rev. B 81, 245204 (2010).
 ⁴⁰ D. Han, Y. Y. Sun, J. Bang, Y. Y. Zhang, H.-B. Sun, X.-B.
- Li, and S. B. Zhang, Phys. Rev. B 87, 155206 (2013).
- ⁴¹ B. G. Mendis, M. D. Shannon, M. C. J. Goodman, J. D. Major, a. a. Taylor, D. P. Halliday, and K. Durose, Journal of Physics: Conference Series 471, 012014 (2013).
- ⁴² T. Gokmen, O. Gunawan, T. K. Todorov, and D. B. Mitzi, Applied Physics Letters 103, 103506 (2013).