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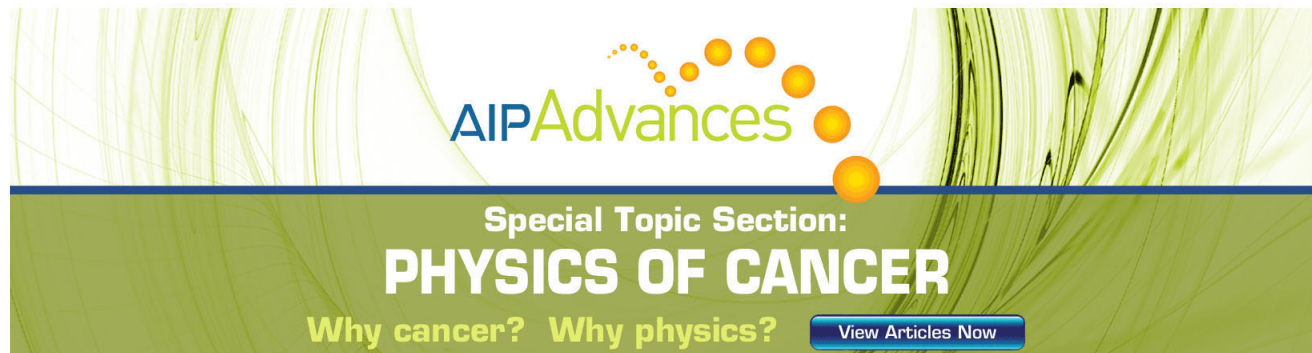
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Bandgap engineering of ZnSnP_2 for high-efficiency solar cells

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ZnSnP_2 , an absorber material for solar cells, transitions from an ordered chalcopyrite to a disordered sphalerite structure at high temperatures. We investigate the electronic structure of both phases, combining a screened hybrid density functional with the special quasi-random structure method. We predict a bandgap reduction of 0.95 eV between the ordered and fully disordered materials. Experimental reports are consistent with partial disorder. Tuning of the order parameter would lead to a family of ZnSnP_2 phases with bandgaps ranging from 0.75 eV to 1.70 eV, thus providing graded solar cell absorbers from a single material system. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4730375>]

Ternary chalcopyrite structured semiconducting compounds with the general valence type I-III-VI₂ (where I = Cu, Ag; III = Al, Ga, In, and VI = S, Se, or Te) have long been investigated due to their applications in optoelectronics, non-linear optics, and as light absorbers in solar cells.¹ This ongoing, focused research effort has produced the thin-film absorber material Cu(In,Ga)Se_2 , which can achieve solar conversion efficiencies of up to 20.3%.² Recently, however, the relative expense and scarcity of In and Ga have motivated a drive for earth abundant materials suitable for large-scale commercialisation.³

Recent progress has been made in the exploitation of quaternary I₂-II-IV-VI₄ materials such as $\text{Cu}_2\text{ZnSnS}_4$.⁴ However, comparatively little attention has been focused on the II-IV-V₂ (II = Zn, Cd; IV = Si, Ge, Sn, and V = N, P, As, or Sb) chalcopyrite structured materials, which offer additional chemical flexibility. ZnSnP_2 , which crystallizes in the chalcopyrite structure, has been reported to possess a bandgap of 1.68 eV,⁵ which is close to the optimum bandgap of 1.5 eV for a single-junction solar cell.

ZnSnP_2 undergoes an order/disorder transition at ~990 K from the chalcopyrite (henceforth denoted as CH-ZSP) structure to a disordered sphalerite structure (SP-ZSP), Figure 1.⁶ In SP-ZSP, the Sn and Zn atoms are randomly distributed over the cation sub-lattice, and the disordered phase has been reported to exhibit a bandgap ranging from 1.22 eV to 1.38 eV.^{5,7} The phenomenon of tunable disorder is well known for semiconductor alloys.⁸

Unusually for a chalcopyrite structured material, ZnSnP_2 does not display any tetragonal distortion (i.e., $c = 2a$), and so the lattice constant for both the chalcopyrite and cubic sphalerite systems is nearly perfectly matched. This opens up the possibility of fabricating a graded multi-junction solar cell using the ordered chalcopyrite as the top layer, with progressively more disordered layers underneath, free from lattice matching problems.⁷ However, for this to be achieved the relationship between

cation ordering and the physical properties of interest must be fully understood.

In this letter, we demonstrate, based on hybrid density functional theory (DFT), that: (1) the calculated bandgap for CH-ZSP is 1.73 eV, which is close to the experimental value of 1.68 eV; (2) the bandgap of the fully disordered SP-ZSP is ~0.75 eV, much lower than previous experiments have suggested; and (3) the order/disorder transition temperature for fully disordered S-ZSP is above 1000 K. Our results suggest that the “disordered” sphalerite structures reported in experiments are not *fully* disordered, but consistent with about ~30%–40% disorder on the cation sublattice. Careful tuning of the growth conditions could be used to engineer ZnSnP_2 with a range of bandgap energies between 1.7 eV and 0.75 eV.

All DFT calculations were performed using the VASP code,⁹ with the projector augmented wave (PAW)¹⁰ approach. The calculations were performed using the screened hybrid functional developed by Heyd, Scuseria,

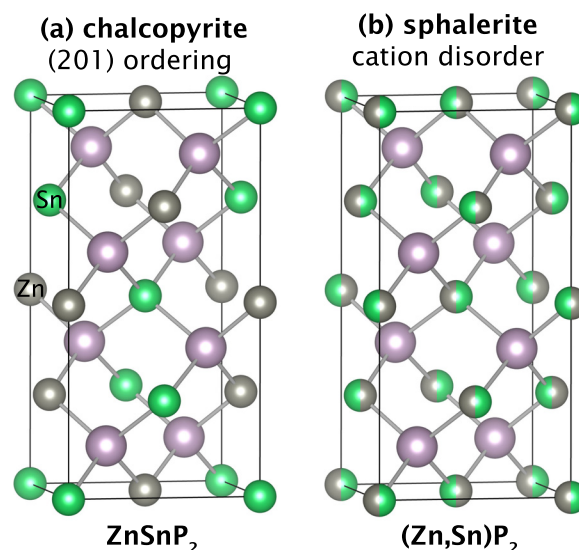


FIG. 1. Schematic showing the (a) ordered chalcopyrite and (b) disordered sphalerite structures of ZnSnP_2 .

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and Ernzerhof (HSE06)¹¹ in which a percentage of the exact non-local Fock exchange ($\alpha = 25\%$) is added to a semi-local functional,¹² with a screening of $\omega = 0.11$ bohr⁻¹ applied to partition the Coulomb potential into long range and short range terms. HSE consistently produces structural and bandgap data that are more accurate than LDA/GGA and meta-GGA data.^{13–20} A basis set cut-off of 390 eV was used, with atomic forces converged to within 0.01 eV Å⁻¹. The disordered 64 atom SP-ZSP cell was generated based on the special quasi-random structure (SQS) approach.²¹ An alternative approach could involve the explicit consideration of all symmetry inequivalent configurations, e.g., as implemented in the site-occupational-disorder (SOD) method.²²

The calculated a and c lattice parameters for CH-ZSP are 5.67 Å and 11.33 Å, respectively, which are in excellent agreement (within 0.3%) of the experimental lattice constants.²³ The band structure is shown in Figure 2. The valence band maximum (VBM) and the conduction band minimum (CBM) both occur at the Γ point, and the calculated fundamental direct bandgap is 1.74 eV, close to experimental measurements of 1.68 eV.⁵ It is clear from the band structure that there is *significant* curvature of the VBM of CH-ZSP, and that the CBM is less disperse, which is consistent with the observed p -type conductivity of CH-ZSP.²⁴

Confident in the knowledge that this level of theory provides a quantitative description of the geometry and electronic properties of CH-ZSP, we have calculated the disordered SP-ZSP structure, and found that the bandgap at the Γ point was 0.75 eV. This value is considerably less than the bandgaps quoted previously, which range from 1.2 to 1.4 eV. It should be noted that the SQS cell employed in this study represents a *fully* disordered sphalerite, whereas previous experimental measurements of the order parameter indicated $\sim 30\%$ disorder.²⁵ Variations in the extent of disorder can explain the differences in bandgap magnitude as illustrated in Figure 3, assuming a linear dependence.

We have calculated the order-disorder transition temperature, using the relation $T_c = \frac{\Delta H}{\Delta S}$, where ΔH is the energy difference between the CH and SP structure, and ΔS is the configurational entropy of the fully disordered sublattice. From this analysis, we obtain a critical temperature of 1295 K, which is ~ 300 K larger than the measured temperature.⁶ The full extent of the disorder involved in the experi-

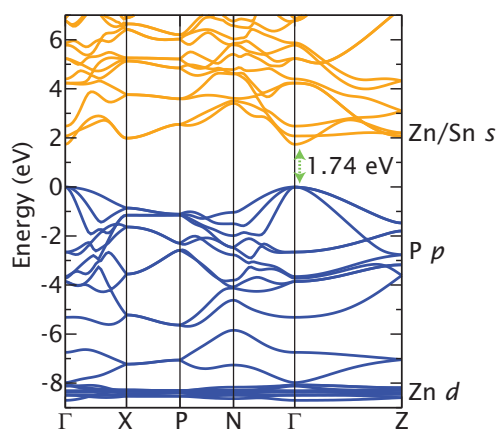


FIG. 2. Calculated band structure for CH-ZSP. The highest occupied state is set to 0 eV.

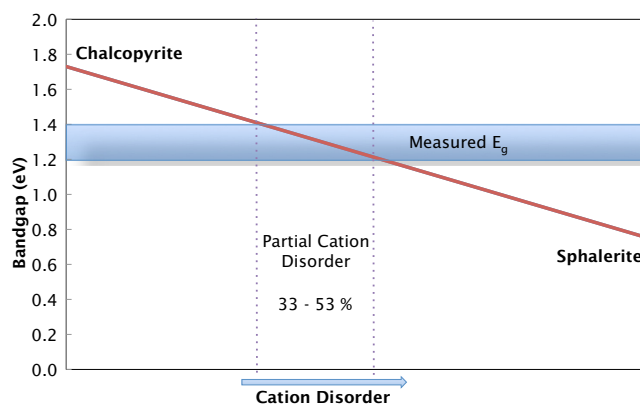


FIG. 3. The relationship between bandgap and disorder on the cation sublattice in ZnSnP₂.

mental order-disorder transitions, however, remains unclear. It is likely that a higher temperature is necessary to produce a fully disordered SP structure, with the smaller bandgap. It is thus evident that a closer examination of the order-disorder transition temperature of ZnSnP₂ is necessary, together with an accurate study of the extent of the disorder in the resulting SP-ZSP samples.

Wei *et al.* have reported that the bandgap narrowing upon onset of disorder is due to the range of cation configurations, which form acceptor-like and donor-like states inside the bandgap.²⁶ To understand the relative band edge alignments of CH-ZSP and SP-ZSP, we have plotted the natural valence band alignment, using the charge neutrality level (CNL) as a reference point within the adopted proposed by Bechstedt and co-workers.²⁷ This analysis predicts that the band alignment between CH-ZSP and SP-ZSP is of “type II,”²⁸ indicating that both electrons and holes will flow into SP-ZSP from CH-ZSP, Figure 4. Both acceptor and donor levels in SP-ZSP will be more shallow than in CH-ZSP, which is consistent with the previous explanation of the reduction of the bandgap by the variety of cationic configurations in disordered SP-ZSP,²⁶ i.e., a mixture of (Sn₃Zn), (Sn₂Zn₂), and (SnZn₃) tetrahedra.

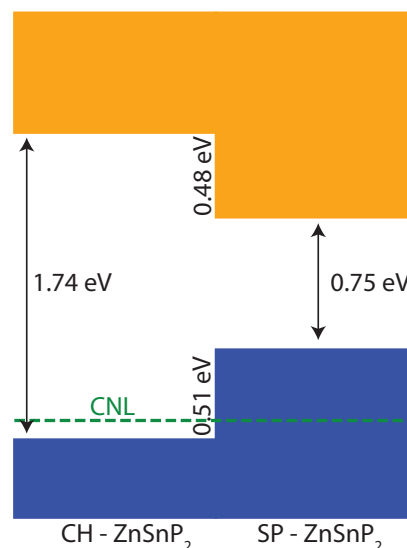


FIG. 4. Calculated valence band alignment of CH-ZSP and SP-ZSP. The dashed line indicates the calculated CNL.

The ability to produce materials with *controlled* disorder has been discussed recently for the case of CdIn_2S_4 spinels,²⁹ and it is expected that a careful modification of the synthesis temperature, or of the cooling rate after synthesis, could be used to tune the magnitude of the bandgap, producing a layered multi-junction solar cell. The use of a single compound such as ZnSnP_2 avoids issues related to variations in crystal structure and stoichiometry that affect other multi-junctions.

In summary, we have provided microscopic insights into the ordered and disordered phases of ZnSnP_2 , and in particular, how control of the cation distribution may lead to bandgap engineering over a 1 eV range, which could be exploited in multi-homojunction solar cells.

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