

Predicting and tuning the defect-tolerance of photovoltaic absorbers from electronic structure: A case study with enargite (Cu_3AsS_4) and bournonite (CuPbSbS_3)

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Defects play a decisive role on device performance... famed defect-tolerance of MAPI... crucial property for a new PV technology to be efficient and commercially viable solar cell technology... In this study we use electronic structure calculations to infer the likely performance of solar cells made from candidate absorber materials enargite and bournonite based on their defect-physics and propose synthesis conditions to promote defect properties that would be beneficial for photovoltaic applications.

New plan: Predict defect formation energy, transition levels and phase diagrams, use Jie's setup to determine processing conditions to raise formation E of deep defects or to encourage defect-pairs to 'clean up' the band gap - use principles from Aron/ Zunger's review + Ji-Sang/ Sunghyun/ Zijuan's review (see discussion at end re not just mid gap, but also transition paths for effective non-rad recombination that are important?). Also discuss more general principles and recipes for defect-tolerance? Bonding character of band extrema, dielectric constant, role of multivalence. Complementary measurements from David's group if possible?

Run enargite and bournonite first, only stephanite if time permits?

Enargite

- Devices fabricated already
- Similar bonding character (p-d repulsion) to CIS, CZTS
- Also explore impact of multivalence of As

Bournonite

- Interest for thermoelectrics and David Mitzi's group
- Role of heavy polarisable species like Pb on defect physics?

Revisit Sunghyun's work for CZTS (SRH without mid-gap states in CZTS and role of multivalence and lone pairs): <http://pubs.acs.org/doi/abs/10.1021/acsenergylett.7b01313>

And Ji-Sang/ Sunghyun/ Zijuan's review:

1 Introduction

We recently identified naturally-occurring minerals as candidate absorber layers for thin-film photovoltaic (PV) devices¹, including enargite (Cu_3AsS_4) and bournonite (CuPbSbS_3). In addition to possessing many desirable optoelectronic properties for a solar cell absorber layer, these materials may

also exhibit ferroelectricity. For this reason, the materials are referred to as candidate 'photoferroics'^{2–4}. Exploiting ferroelectricity in photoactive materials could allow novel PV phenomena such as the anomalous and bulk photovoltaic effects to provide new pathways to high-efficiency PV devices by allowing for larger photovoltages and with enhanced carrier separation from internal electric fields to suppress

electron-hole recombination⁴.

** + also refer to paper suggesting contact materials for p-n junctions if complete** To accelerate the development of PV devices, we have also proposed suitable contact materials for enargite and bournonite based on lattice matching and electronic band offsets². To our knowledge, a solar cell device has not yet been fabricated from bournonite and only one study in the literature has synthesised a full PV device using enargite as the absorber layer⁵. In this study the absorber layer was solution processed and device architecture similar to that developed for CIGS technology was used. There is also technological interest in bournonite for its potential applications as a thermoelectric^{6,7}.

A fundamental principle of thin-film PV technology is to utilise low-cost and low-temperature fabrication methods to dramatically reduce the energy payback time of solar power systems; in contrast to those of conventional crystalline silicon modules. Such fabrication methods typically result in materials with a large number of imperfections such as intrinsic point defects and grain boundaries. It is therefore crucial for the performance of the material to be sustained despite such imperfections. The defect-physics of an absorber material plays a crucial role in determining its performance in a thin-film solar cell device.

May need to modify this paragraph wrt discussion in Ji-Sang/ Sunghyun/ Zijuan review re importance of transitions that facilitate effective non-rad recomb It is important that intrinsic defects in a PV material produce shallow defect levels relative to the band edges of the perfect material. Shockley-Read-Hall recombination is known to be particularly detrimental to device performance and is associated with deep-level defects, which have been referred to as 'killer-centres' for their ability to cause rapid recombination even at very low concentrations⁸. Furthermore, low concentrations of shallow defects can have the beneficial effect of self-doping the material to improve electrical conductivity for better carrier transport and extraction of charge-carriers from the PV material to do electrical work⁹. The rapid progress in device efficiencies of hybrid perovskite solar cells is largely attributed to the particularly beneficial defect properties of the material, often referred to as its 'defect-tolerance'^{10–12}. In this work therefore, we aim to assess the likely performance of enargite (Cu_3AsS_4) and bournonite (CuPbSbS_3) solar cells based on the defect-physics of the absorber materials. We also explore options for tuning the defect properties of the materials for PV applications using principles of defect-tolerance determined from decades of research on other PV materials^{9,13}.

To our knowledge, currently there have been no studies examining the defect-physics of enargite, but experimental measurements on natural samples have measured p-type conductivity^{14,15}. The material may therefore be intrinsically p-type, or more easily doped p-type. We therefore could expect shallow acceptor-type defects with low formation energies. First principles density functional theory (DFT) defect calculations have been performed for bournonite using a semilocal functional within the generalised-gradient approximation (GGA)⁷, where the authors predict that the material will be intrinsically p-type and that it will be difficult to dope n-type based on the predicted high concentration of acceptor-type defects. However, there is some contradiction in the literature with measurements on two natural samples of bournonite measuring n-type conductivity¹⁵. This disagreement could either be explained by extrinsic impurities in the natural samples that were not considered in the theoretical study, or due to the limitation of the level of theory used.

** condense next two paragraphs **

In many cases standard DFT methods often fail at the description of the electronic structure of a defective crystal. The GGA severely underestimates the band gaps of semiconductors and insulators¹⁶. This is the case for bournonite with a band gap of 0.385 eV predicted using the GGA and including spin-orbit interaction⁶, while reported experimental measurements of the band gap range from 1.01 to 1.31 eV^{15,17,18}. Defect formation energies are in general affected by this band-gap problem in two ways. Firstly, defect states may be predicted to be within the continuum of host states when the band gap is underestimated but actually be within the band gap if the band-gap problem is corrected. The result of this incorrect placement of the defect level is that electron-occupied defect states can erroneously spill into the conduction band or similarly hole defects could spill into the valence band. The calculated charge density associated with these defects would then be incorrect, resulting in an uncontrolled error in the value obtained for the defect formation energy. For charged defects, there is an additional source of error due to the formation energy being dependent upon the Fermi level, E_F . E_F is bounded by the band-edge energies and so when the band gap is changed the range of formation energies between the valence band maximum and conduction band minimum is altered¹⁹.

It has been shown for GaN that the use of semilocal functionals for the calculation of defect formation energies with band edges shifted to account for the underestimation of the band gap can account for the majority of the error associated with this level of theory and produce results that are qualitatively (or even quantitatively) correct. However, important

physics can be missed by these lower-computational-cost functionals in cases when carrier localisation occurs and there can be significant differences in atomic relaxations (**cite** DOI: 10.1038/s41524-017-0014-2). The band gap problem can be addressed by going beyond DFT. One such method is hybrid-DFT. Hybrid approaches incorporate a certain amount of screened exact exchange from the Hartree-Fock approximation with DFT exchange-correlation functionals. Hybrid functionals, such as the HSE06 functional²⁰ used in this study have been shown to produce band structures in much better agreement with experiment and provide a much more reliable description of charge localisation¹⁶.

We therefore aim to resolve the discrepancy in the literature on the defect physics of bournonite through the use of full hybrid functional calculations of the defect formation energies, before investigating the possibility of altering the chemical potentials of the components during the synthesis to tune the defect physics of these two materials.

1.1 Defect tolerance papers

MAPbI₃¹¹, CuInSe₂¹³, Cu₃N²¹, high-throughput study²² and Aron's review⁹ + Joe Berry's work on MAPI defect-tolerance¹² + Ji-Sang/ Sungyun/ Zijuan review *add citation when available*

2 Computational details

2.1 Density functional theory defect calculations

Density functional theory (DFT) calculations in this study are all performed using the FHI-aims all-electron electronic structure code, which is an implementation of DFT based on numeric atom-centered orbital basis sets with a linear-scaling approach to hybrid functionals^{23–27}. We use the HSE06 functional²⁰ with spin-orbit coupling as implemented in FHI-aims²⁸.

Geom opt.: Default tight basis (pre-relax with light and use intermediate for Pb? - state that compared total E of unit cell with intermediate and tight), converge forces to within 0.5×10^{-3} per atoms relax supercells first using gamma point k-mesh, then repeat with $2 \times 2 \times 2$ k-grid with SOC. hse for enargite and hse+D for bournonite (dispersion correction to correct for van der Waals interactions of Pb lone pairs)

In this study, we relax the volume of unit cells of each structure because even slight differences in cell volume (for HSE06-optimised structures) relative to the experimental lattice parameters used in our previous study¹ could result in unphysical defect relaxations to compensate for the strain.

comment on lattice param difference wrt XRD data when using hse volume relaxation We then use the supercell method in order to calculate defect formation energies using periodic DFT calculations²⁹. We construct a $2 \times 2 \times 2$ simple cubic supercell of the optimised 16 atom enargite unit cell and a 96 atom body-centred cubic supercell of the optimised 24 atom bournonite unit cell. This supercell for bournonite was chosen to be more computationally feasible than a $2 \times 2 \times 2$ simple cubic supercell, but also resulted in a larger packing fraction of 1.093, compared to just under 1 **check** for the 192 atom $2 \times 2 \times 2$ simple cubic supercell.

+ present visuals of supercells here + refer to Transformer libraries (mention repo in open access statement?) and maybe pylada³⁰ for interstitials? to introduce all symmetry unique defects in the supercells

2.2 Finite-size corrections for charged defect supercells

Janak's test in SI to confirm validity of potential alignment correction step.^{31 32}

** see pylada paper **³⁰

Of the various correction schemes available^{???}, we have used the Lany-Zunger scheme¹⁹ as implemented in the AIDE software package[?], which has been interfaced with the FHI-aims electronic structure software package.

** Add more detailed methodology of defect calculations with FHI-aims, $V_{at}^{es}(0)$ as Hartree potential at each atom excluding atom itself to avoid divergence at core, refer to aims paper eqn 62 and 66? <https://doi.org/10.1016/j.cpc.2009.06.022>

- Potential alignment in FHI-aims: core levels extracted from eigenvalue list, separated by Wyckoff position, averaged and shift between neutral and charged supercell extracted?
- Image charge correction: static dielectric constant calculated with FHI-aims (method outlined below) and Ewald solver (from pylada or in-built from aims?) to simulate the charged defect in a dielectric continuum
- Band-filling corrections for shallow defects? - later consideration?

²⁹

+ cite AIDE repo

2.3 Calculation of dielectric constants

In a solid in the absence of free dipole rotations, the dielectric response to a static perturbing electric field, such as that from a charged defect within the host lattice, is described by the re-organisation of the electronic density (electronic polarisability), or from the motion the ions relative to one another (ionic polarisability). The static limit of the former, which we denote by ϵ_∞ , is the $\omega \rightarrow 0$ limit of the optical dielectric function, $\epsilon(\omega)$. The latter, which we denote as ϵ_{ionic} , is related to the phonon density of states. The static dielectric constant of a material is composed of contributions from both response mechanisms, as shown by equation 1.

$$\epsilon = \epsilon_\infty + \epsilon_{\text{ionic}} \quad (1)$$

We take the static limit of ϵ_∞ from the optical dielectric function calculated using the random phase approximation as implemented in FHI-aims in a previous study¹

Outline DFPT dielectric calculation with FHI-aims for ionic component (using pbe and justify based on GGA found to be accurate for atomic structure/ phonon calcs) (cite ref x3 from pg 238 of aims manual)... unless having to use VASP here (pbesol, no SOC and (underscore)d pseudopotential for Pb in bournonite)? (check with Honghui nearer the time and update intro to this section to include VASP if need be)

3 Results and discussion

3.1 Chemical potential range

Use CPLAP or talk to Stephan/ Jie? or in-built in AIDE?

****cite use of CPLAP****

Present calculated phase diagrams used to determine suitable range of accessible chemical potentials to synthesise enargite and bournonite. Exptl. reference for enargite³³. And compare to range used in GGA bournonite defects study SI (just under defect formation E vs Ef plots)?⁷

May need to project onto 2D face of polyhedra for quaternary bournonite? (c.f. Chen paper for CZTS, DOI: 10.1002/adma.201203146)

See description of chemical potentials in pylada paper³⁰

Outline how competing phases were selected from materials project: stable and any stable compounds with energies up to 100 meV above the hull.

Paper on metastability and compounds being synthesisable if within certain range for E above hull... also cite if bournonite is still 3 meV above the hull on hse phase diagram: <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5262468/>

3.2 Defect formation and ionization

Equation for equilibrium defect concentration from formation energies

Present defect transition levels

Present concentration maps for defects (and pairs?) w.r.t Fermi energy and accessible chemical potential range using Jie's setup

3.3 Tuning the impact of defects

Discuss options for tuning defect-tolerance: chemical potentials to suppress deep level defects and/ or encourage benign defect pairs^{13,9}

'Thus, all other things being equal, positively charged defects electronproducing donors have higher concentration in p-type environment EF near Ev, whereas negatively charged defects hole-producing acceptors have higher concentration in n-type environment EF near Ec. Furthermore, cation-substituting impurities have higher concentrations under cation-poor growth condition cation most negative, whereas anion-substituting impurities have higher concentrations under anion-poor growth conditions anion most negative.'³² Summarised as 'doping rules'³⁴

Comment on likely n- or p-type conductivity based on defect physics and doping rules, relate to work on predicting device architecture?

Comment on any relationships observed for predicting formation energy or depth of defect level (former more straightforward to infer possibly?)

Also mention Sunghyun/ Ji-Sang's recent works discussing possibility of non-rad recombination without mid gap states (links to lone pairs and multivalence in CZTS)

Also discuss implications on defect-tolerance from dielectric constants of the materials? (link to dielectric function review)

4 Summary and outlook

(In a very ideal world!) - Determine synthesis processing conditions (chemical potentials) for optimal defect physics for PV for the two materials with experimental cross referencing for bournonite + refer to paper for suggested device architectures

Comment on multivalence of As in enargite and polarisability of Pb in bournonite + low thermal conductivity of bournonite⁶ could mean it will be 'phonon-protected from non-radiative recombination at defects as is postulated for MAPI? **check with WMD how work/ understanding is developing here**

Broader impact - suggests similar analysis for other emerging PV technology could accelerate the optimisation of device development?

Important areas of further work - (firstly experimental testing of conditions suggested here) but secondly, due to computational expense of defect calculations, determination of trends for the prediction of depth of defect level would be immensely powerful for materials screening for PV. Refer to work by Vladan, Prashun and Anuj with pylada and Rachel Kurchin at MIT for defect-tolerance metrics.²² Also summarise any discussion on possible trends mentioned earlier in this work, e.g. role of multivalence in As and polarisability of Pb?

Discussion of role of ionicity from first page RHS of Joe Berry's work on MAPI defect-tolerance

Ideas from Scanlon group meeting: consider Cu:S ratio as explanation for pronounced p-d repulsion in enargite and CuInSe₂ but not other compounds, CB and VB level w.r.t vacuum more relevant than character of band extrema? Generally a coincidence that defect-tolerant systems tend to have both characteristics? (obtain this for sulfosalts and compare)

5 Open access statement

Link to defects with transformer repo + pylada if used for interstitials/ for ewald solver? Upload defects data to a repository? + link to my wiki if instructions for finite-size corrections with FHI-aims are here? (more likely... link to AIDE repo and upload calculation data to a repo)

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David Scanlon for discussions (or not if author with AIDE)

Nathaniel Raimbault for discussions re dfpt dielectric if used in the end?

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References

- 1 S. K. Wallace, K. L. Svane, W. P. Huhn, T. Zhu, D. B. Mitzi, V. Blum and A. Walsh, *Sustainable Energy Fuels*, 2017, **1**, 1339–1350.
- 2 V. M. Fridkin, *Photoferroelectrics*, Springer-Verlag Berlin Heidelberg, 1979.
- 3 B. I. Sturman and V. M. Fridkin, *Photovoltaic and Photo-refractive Effects in Noncentrosymmetric Materials*, Gordon and Breach Science Publishers, 1992.
- 4 K. T. Butler, J. M. Frost and A. Walsh, *Energy and Environmental Science*, 2015, **8**, 838–848.
- 5 S. A. McClary, J. Andler, C. A. Handwerker and R. Agrawal, *J. Mater. Chem. C*, 2017, **5**, 6913–6916.
- 6 Y. Dong, A. R. Khabibullin, K. Wei, J. R. Salvador, G. S. Nolas and L. M. Woods, *Chem Phys Chem*, 2015, **16**, 3264–3270.
- 7 A. Faghaninia, G. Yu, U. Aydemir, M. Wood, W. Chen, G.-M. Rignanese, G. J. Snyder, G. Hautier and A. Jain, *Phys. Chem. Chem. Phys.*, 2017, **19**, 6743–6756.
- 8 A. M. Stoneham, *Reports on Progress in Physics*, 1981, **44**, 1251–1295.
- 9 A. Walsh and A. Zunger, *Nature Materials*, 2017.
- 10 W.-J. Yin, T. Shi and Y. Yan, *Applied Physics Letters*, 2014, **104**, 063903.
- 11 R. E. Brandt, V. Stevanović, D. S. Ginley and T. Buonassisi, *MRS Communications*, 2015, **5**, 265–275.
- 12 K. X. Steirer, P. Schulz, G. Teeter, V. Stevanovic, M. Yang, K. Zhu and J. J. Berry, *ACS Energy Letters*, 2016, **1**, 360–366.
- 13 S. B. Zhang, S.-H. Wei, A. Zunger and H. Katayama-Yoshida, *Physical Review B*, 1998, **57**, 9642–9656.
- 14 T. Pauporte and D. Lincot, *Advanced Materials for Optics and Electronics*, 1995, **5**, 289–298.
- 15 B. Durant and B. A. Parkinson, 2016 IEEE 43rd Photovoltaic Specialists Conference (PVSC), 2016.
- 16 A. Alkauskas, M. D. McCluskey and C. G. Van de Walle, *Journal of Applied Physics*, 2016, **119**, 181101.
- 17 H. Dittrich, A. Stadler, D. Topa, H.-J. Schimper and A. Basch, *Physica Status Solidi (a)*, 2009, **206**, 1034–1041.
- 18 K. Wei, J. Martin, J. R. Salvador and G. S. Nolas, *Crystal Growth & Design*, 2015, **15**, 3762–3766.
- 19 S. Lany and A. Zunger, *Model. Simul. Mater. Sci. Eng.*, 2009, **17**, 084002.
- 20 J. Heyd, G. E. Scuseria and M. Ernzerhof, *The Journal of Chemical Physics*, 2003, **118**, 8207–8215.
- 21 A. Zakutayev, C. M. Caskey, A. N. Fioretti, D. S. Ginley, J. Vidal, V. Stevanovic, E. Tea and S. Lany, *The Journal of Physical Chemistry Letters*, 2014, **5**, 1117–1125.
- 22 R. E. Brandt, J. R. Poindexter, P. Gorai, R. C. Kurchin, R. L. Z. Hoye,

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- L. Nienhaus, M. W. B. Wilson, J. A. Polizzotti, R. Sereika, R. Žaltauskas, L. C. Lee, J. L. MacManus-Driscoll, M. Bawendi, V. Stevanović and T. Buonassisi, *Chemistry of Materials*, 2017, **29**, 4667–4674.
- 23 V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, *Computer Physics Communications*, 2009, **180**, 2175–2196.
- 24 X. Ren, P. Rinke, V. Blum, J. Wieferink, A. Tkatchenko, A. Sanfilippo, K. Reuter and M. Scheffler, *New Journal of Physics*, 2012, **14**, 053020.
- 25 S. V. Levchenko, X. Ren, J. Wieferink, R. Johanni, P. Rinke, V. Blum and M. Scheffler, *Computer Physics Communications*, 2015, **192**, 60–69.
- 26 A. C. Ihrig, J. Wieferink, I. Y. Zhang, M. Ropo, X. Ren, P. Rinke, M. Scheffler and V. Blum, *New Journal of Physics*, 2015, **17**, 093020.
- 27 V. Havu, V. Blum, P. Havu and M. Scheffler, *Journal of Computational Physics*, 2009, **228**, 8367–8379.
- 28 W. P. Huhn and V. Blum, *arXiv preprint: 1705.01804*, 2017.
- 29 S. Lany and A. Zunger, *Model. Simul. Mater. Sci. Eng.*, 2009, **17**, 084002.
- 30 A. Goyal, P. Gorai, H. Peng, S. Lany and V. Stevanovic, *arXiv preprint:1611.00825v1*, 2016.
- 31 J. F. Janak, *Phys. Rev. B*, 1978, **18**, 7165–7168.
- 32 C. Persson, Y.-J. Zhao, S. Lany and A. Zunger, *Phys. Rev. B*, 2005, **72**, 035211.
- 33 Z. T. Gasanova, L. F. Mashadieva, Y. A. Yusibov and M. B. Babanly, *Russian Journal of Inorganic Chemistry*, 2017, **62**, 591–597.
- 34 A. Zunger, *Applied Physics Letters*, 2003, **83**, 57–59.