Faraday Discussions

Cite this: *Faraday Discuss.*, 2022, **239**, 375

DISCUSSIONS

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Materials design and bonding: general discussion

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DOI: 10.1039/d2fd90058k

Nada Benhaddou opened the discussion of the paper by Jiang Tang: You have performed the annealing in an unsealed graphite box. I am wondering if there is a reason behind this choice. Have you ever tried with a sealed one and noticed a difference between the two systems?

Jiang Tang answered: Thanks for your question. We use an unsealed graphite box for the annealing of Se films because we want to achieve rapid cooling to reduce the sublimation of Se atoms during annealing. The open system may be more conducive to rapid cooling of the Se films. We also agree that a sealed system can reduce the degradation of Se films during annealing to some extent, but we haven't conducted a comparative test of annealing with different graphite boxes. Thank you for your suggestion. We will try to anneal our Se films with a sealed graphite box later.

Aron Walsh remarked: It is nice to see a historic system, such as Se, being revisited for photovoltaics. I am curious that the older literature refers to Se as an indirect band gap material, while you refer to it as being a direct band gap material. Do you know which is the case?

Jiang Tang answered: Thank you very much for your question. According to previous studies, trigonal selenium is considered to be a direct band gap semiconductor at room temperature.[1,2] A direct band gap semiconductor does not need phonons to participate in the photoelectric conversion, and its power conversion efficiency is usually higher than that of an indirect band gap semiconductor, which is also the advantage of trigonal selenium as a photovoltaic material.

[1] J. Treusch and R. Sandrock, *Phys. Status Solidi B*, 1966, **16**, 487.
[2] S. Tutihasi and I. Chen, *Phys. Rev.*, 1967, **158**, 623.

Jonathan D. Major asked: Prior work on selenium solar cells used a tellurium wetting layer in order to achieve the correct morphology after annealing.[1] Have you had to use that for your process or is the selenium deposited directly onto the zinc oxide? Does the ZnO play a role in achieving good coverage?

[1] T. K. Todorov, S. Singh, D. M. Bishop, O. Gunawan, Y. S. Lee, T. S. Gershon, K. W. Brew, P. D. Antunez and R. Haight, *Nat. Commun.*, 2017, **8**, 682.

Jiang Tang replied: Thanks for your question. Compared with the previous work, our Se film is directly deposited on the ZnO layer. We believe that the slight reaction at the Se/ZnO interface during rapid thermal annealing (RTA) can release the stress at the interface and improve the coverage of the Se film (Fig. S2 in the ESI of our paper, **https://doi.org/10.1039/d2fd00070a**). We also tried to prepare Se films on other n-type materials (like CdS and TiO_2), but due to a lack of stress relief at the interface, the Se films would detach from the substrate and pinholes would form in the film due to excessive stress in the annealing process. So we think the ZnO layer plays a role in achieving good coverage of the Se film.

Mirjana Dimitrievska queried: You mentioned that Si can be used as a bottom solar cell with a Se-based solar cell on top. Have you tried growing Se films on Si wafers and, if so, how successful was it?

Jiang Tang replied: Thanks for your question. We have not yet integrated our Se cell with silicon cells or fabricated Se films on Si wafers. However, we plan to prepare our further-optimized Se solar cell on a Si bottom cell in the future.

David J. Fermin commented: It is unusual to see crystal reorientation in a thin film promoted by a fast thermal treatment instead of a slow annealing step. Could you elaborate on the mechanism and factors behind this observation?

Jiang Tang answered: Thanks for your question. In fact, we believe that the rate of crystal reorientation is closely related to the temperature of the treatment. Under a certain temperature, the atoms gain enough energy to break the bonds and be rearranged, leading to crystal reorientation. Furthermore, under higher temperatures, the thermal motion of the atoms is more intense, and the crystal reorientation is faster. So, as long as the temperature is high enough, we can achieve crystal reorientation through rapid thermal annealing. Actually, rapid thermal annealing is a common method for promoting the crystallization of chalcogenide photovoltaics with high saturated vapor pressure, such as Sb_2Se_3 and GeSe, *etc.*[1–3]

[1] X. Wen, C. Chen, S. Lu, K. Li, R. Kondrotas, Y. Zhao, W. Chen, L. Gao, C. Wang, J. Zhang, G. Niu and J. Tang, *Nat. Commun.*, 2018, **9**, 2179.
[2] Y. Lu, K. Li, X. Yang, S. Lu, S. Li, J. Zheng, L. Fu, C. Chen and J. Tang, *ACS Appl. Mater. Interfaces*, 2021, **13**, 46858.
[3] S.-C. Liu, C.-M. Dai, Y. Min, Y. Hou, A. H. Proppe, Y. Zhou, C. Chen, S. Chen, J. Tang, D.-J. Xue, E. H. Sargent and J.-S. Hu, *Nat. Commun.*, 2021, **12**, 670.

Rokas Kondrotas asked: Have you tried any doping strategies for the Se absorber?

Jiang Tang answered: Thank you for your question. We have not tried any doping processes on the Se film yet.

Jake W. Bowers asked: Have you tried making these devices in a substrate configuration with a molybdenum back contact?

Jiang Tang replied: Thank you very much for your suggestion. At present, we have not employed a molybdenum back contact in our device. But we have noticed the mature application of molybdenum electrodes in CIGS and CZTS solar cells, and we plan to introduce it into our device after further optimization of our Se thin film.

Susanne Siebentritt said: Se is very reactive. How stable are these solar cells? Do you keep them in air or in a desiccator?

When you measure again after a week, or a month, do they still show the same efficiency?

Jiang Tang replied: Thanks for your question. Our Se cells have good air stability. In our recent study, we compared the V_{oc} (open-circuit voltage), J_{sc} (short-

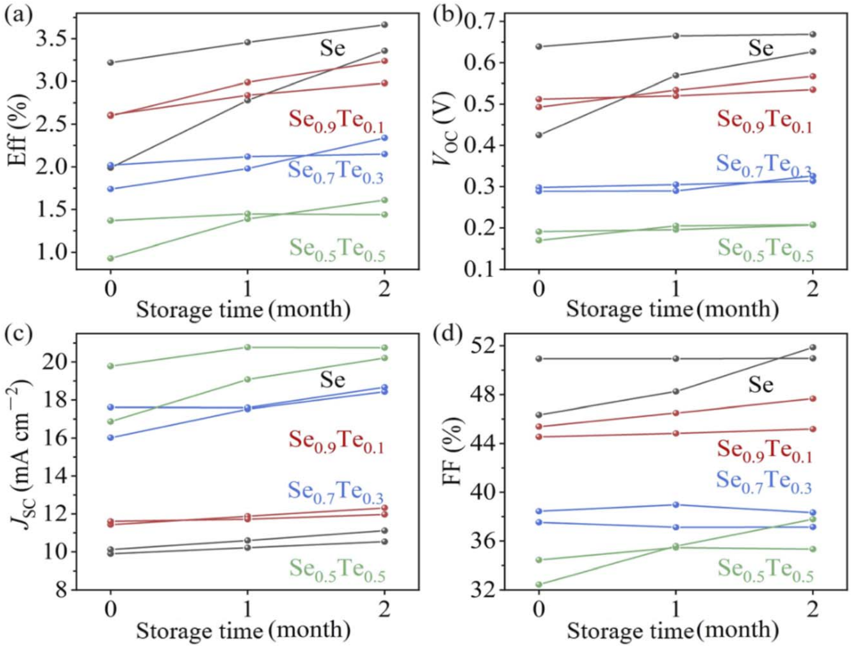

Fig. 1 The PCE (labelled as Eff) (a), V_{oc} (open-circuit voltage) (b), J_{sc} (short-circuit current) (c) and FF (fill factor) (d) of Se_xTe_{1-x} ($x = 1$, 0.9, 0.7, 0.5) cells exposed to air (room temperature 25 °C) for 0, 1, and 2 months. The structure of our Se_xTe_{1-x} solar cell is ITO/ZnO/ Se_xTe_{1-x}/Au. The curves in different colors represent different ratios of Se to Te in the Se_xTe_{1-x} cells ($x = 1$, black; $x = 0.9$, red; $x = 0.7$, blue; $x = 0.5$, green).

circuit current), FF (fill factor) and PCE (power conversion efficiency) of Se_xTe_{1-x} ($x = 1$, 0.9, 0.7, 0.5) cells exposed to air (room temperature 25 °C) for 0, 1, and 2 months.[1] The results show that our Se_xTe_{1-x} solar cells have no obvious deterioration, and that some parameters are even slightly improved. We think these may be related to the stress release in the Se_xTe_{1-x} film (Fig. 1)

[1] J. Zheng, L. Fu, Y. He, K. Li, Y. Lu, J. Xue, Y. Liu, C. Dong, C. Chen and J. Tang, *Front. Optoelectron.*, 2022, **15**, 36.

Sreekanth Mandati asked: You mentioned that the cooling rate in the selenization process was 5 °C per second. How did you control this? Also, there is a sub-bandgap edge in the Tauc plot, which is ascribed to oxidation of selenium. If you chose to do selenization in a tube furnace with prior evacuation, followed by filling with N_2, how did you expect the oxidation of Se?

Jiang Tang replied: Thanks for your question. We achieved rapid cooling through opening the thermal insulation cover of the RTA chamber and placing it at a lower ambient temperature (20 °C). At the end of the annealing process, the RTA chamber gets cooled at a rate of about 5 °C per second. When the temperature of the RTA chamber gets close to the ambient temperature, the cooling rate gradually decreases.

To the other question: Thanks for your suggestion. I think using selenium powder to react with the oxygen remaining in the tube furnace is a good deoxygenation method worth trying, and will not introduce impurities. We expect this method to reduce the oxidation of Se films during annealing.

Mirjana Dimitrievska opened a general discussion of the paper by Moohit Sood: Regarding your record V_{oc} solar cell device, you mentioned that the J_{sc} and FF are not as good. Why is that, and what are your next steps to improve these parameters?

Mohit Sood responded: The record V_{oc} device was prepared with an absorber having an average [Ga]/[Ga + In] concentration of 0.6 measured by energy-dispersive X-ray spectroscopy at 20 kV. When looking at the cross-section of this device, we observed a bilayer structure within our absorber. We speculate that this leads to bad transport in our device and, therefore, a lower J_{sc} and FF. In the next step, we are trying to make absorbers with a lower average [Ga]/[Ga + In] ~ 0.2, as these absorbers are observed to not have a bilayer structure within our absorbers. Preliminary results already show improvements in the device J_{sc} and FF.

Charlotte Platzer Björkman queried: Do you think it is likely that the minor additional annealing time between, for example, the 1000 cycle deposition and 1200 cycle deposition can cause the observed change in the quasi-Fermi level (qFL) splitting?

Mohit Sood replied: We have recently investigated the impact of annealing $Cu(In,Ga)S_2$ absorbers coated with 1000 deposition cycles of (Zn,Sn)O in a nitrogen environment. In that study, we observed an improvement in the quasi-

Fermi level splitting for 15 minute and 30 minute annealing times, and a loss in quasi-Fermi level splitting for higher annealing duration. These results suggest that annealing does play a role and might be the reason why we see a improvement in quasi-Fermi level splitting between 1000 cycles and 1200 cycles.

Charlotte Platzer Björkman asked: Does the buffer layer thickness influence the qFL splitting? What would you see regarding the qFL if increasing numbers of CdS buffer layers were deposited, for example?

Mohit Sood answered: The buffer thickness can influence the quasi-Fermi level splitting if it alters the radiative and non-radiative recombination channel within the device.

Regarding the increase in CdS buffer layer thickness, I think it is very hard to speculate what will happen. Maybe with a thicker buffer layer, we might get more band bending in the absorber. This could lead to a modification in the recombination channels within the space charge region or close to the interface. However, as to what will be the impact on the quasi-Fermi level splitting, this will depend upon the nature of the non-radiative recombination centers within this region.

Susan Schorr commented: With regard to the formation of vacancy phases when the chalcopyrite phase becomes Cu-poor, $CuGaS_2$ is special in comparison to $CuGaSe_2$ (as well as $CuInSe_2$ and $CuInS_2$). According to our experimental findings,[1] when $CuGaS_2$ becomes Cu-poor, GaS is formed instead of a vacancy phase. You report in your paper (**https://doi.org/10.1039/d2fd00046f**) that you have a high Ga content in $Cu(In,Ga)S_2$ towards the back contact. Could it be possible that GaS is formed and may cause problems for your device?

[1] C. Stephan, S. Schorr and H.-W. Schock, *Mater. Res. Soc. Symp. Proc.,* 2009, **1165**, 908.

Mohit Sood answered: Thank you for the insight. In both the SIMS and quant mapping on the cross-section of the absorber using energy dispersive X-ray analysis, we have observed a Ga enrichment and an In deficiency towards the molybdenum contact (back side) in the sample. However, we did not observe any Cu deficiency towards the molybdenum, which might, *prima facie*, suggest there is no GaS phase forming at the back. To investigate it further, we will investigate the absorber from the rear side using Raman spectroscopy to gain further insights into the possible phases forming at the back.

Rafael Jaramillo remarked: For the buffer deposited at 105 °C, the PL emission curves look to be simply down-shifted. It seems as if a PL quenching mechanism was added (or the optics changed to make extraction less likely), without changing the emitting material. As opposed to the case of the buffer deposited at 120 °C, in which case the spectrum changed, indicating a change in the emitting material and/or the location of emission within the stack.

Mohit Sood answered: For the buffer deposited at 120 °C, we believe the change in the spectrum comes from the Ga grading within the absorber. Our absorbers are not uniform in terms of composition and they have a slight [Ga]/

[Ga + In] concentration variation. We have observed a slight shift in the PL emission peak depending on the [Ga]/[Ga + In] concentration in the absorber when measuring the same absorber at different spots. Of course, it can be that the location of the emission within the stack also changed after depositing the buffer. This is something that we are investigating now.

Mohit Sood addressed Susanne Siebentritt: Can you please comment on the expected changes in the PL spectrum if we change the buffer thickness? How can this impact the radiative and non-radiative recombination signals in the PL?

Susanne Siebentritt replied: This is not so easy to answer, because many things can happen.

If the buffer has a wide band gap and no absorption in the spectral region of the PL spectrum, and if it is very low doped, the PL should not change with buffer thickness.

If the buffer shows absorption in the spectral region of the PL, it would distort the spectrum and increasingly so with a thicker layer.

If the buffer is sufficiently highly doped: with increasing buffer thickness, a space charge region in the absorber will build up. If we measure the PL with a small spot, the flux will decrease, because we are no longer at open-circuit. If we measure with a large spot, that illuminates the whole sample, so nothing should change.

Another thing to keep in mind: if the buffer has a strong absorption of the excitation light, it would decrease the intensity that reaches the absorber and, thus, decrease the PL. I'm sure there are other effects that I don't have in mind right now.

Marcus Bär asked: In the paper (**https://doi.org/10.1039/d2fd00046f**), you argue that the buffer has to be "dense enough" to protect against sputter damage. Do you have any indications for sputter damage?

Mohit Sood responded: Thank you Marcus for your question. Our claim was based on the R_{sh} values observed for these devices. While we do not have direct proof of sputter damage, we do have indirect indications of sputter damage in our samples. We have performed qFL (intensity calibrated photoluminescence) measurements on absorbers coated with ZnMgO buffer layers using atomic layer deposition and sputtering. In the sputtered ZnMgO buffer samples, we have observed significantly lower qFLs compared to the atomic layer deposited ZnMgO buffer devices. Also, in the resulting devices, we have observed lower R_{sh} in sputtered ZnMgO buffer devices compared to the atomic layer deposited ZnMgO buffer devices.

Sreekanth Mandati said: Your PL curves appear to have the same area under the curve if you subtract the background; how can it be considered as significant PL quenching?

Mohit Sood answered: What we show here is the PL intensity, which takes into account any background correction already. Thus the drop in PL intensity after buffer 1 deposition is essentially due to significant non-radiative recombination increasing after buffer 1 deposition.

Susanne Siebentritt added: Sputter damage does play a role – at least in chalcopyrite solar cells.

Researchers at EMPA have shown that, even with a remote plasma treatment on an absorber with a thin buffer, they already lose some 10 mV in V_{OC} (see ESI of ref. 1 for this measurement).

1 J. Löckinger, S. Nishiwaki, T. P. Weiss, B. Bissig, Y. E. Romanyuk, S. Buecheler and A. N. Tiwari, *Sol. Energy Mater. Sol. Cells*, 2018, **174**, 397.

Raphael Agbenyeke asked: Do you have any idea what the oxidation state of Sn is in ZTO films?

How will a difference in oxidation state (+2, +4) potentially affect the device performance? What Sn precursor was employed?

Mohit Sood answered: We expect Sn to have a +4 oxidation state in (Zn,Sn)O films.

We would rather refrain from commenting anything about the impact of oxidation state (+2, +4) on the device performance.

We used TDMASn as the Sn precursor.

Charlotte Platzer Björkman added: The Sn precursor is $Sn(IV)(N(CH_3)_2)_4$, tetrakis(dimethylamino)tin, *i.e.* +4 oxidation state. As for the oxidation state in the ZTO films, +4 is most likely, but the exact stoichiometry is not easy to determine and generally ZTO is denoted $Zn_{1-x}Sn_xSn_y$. Hydroxides can also be present in the films, as the oxygen precursor is H_2O. The potential influence on the performance of the devices would most likely be a consequence of the band gap of the ZTO and the energy-band lineup. SnO and SnO_2 have different band gap energies, also indirect *vs.* direct, but, in the case of the amorphous ZTO, we assign the band gap energy changes seen as a function of deposition temperature to quantum size effects; see more in ref. 1.

1 J. Lindahl, C. Hägglund, J. T. Wätjen, M. Edoff and T. Törndahl, *Thin Solid Films*, 2015, **586**, 82.

David O. Scanlon remarked: As a community, we do seem to focus on the absorber, and not on the buffer layers or the electron/hole transport layers. So we have a very well characterised absorber, and a well defined buffer (in this case, (Zn,Sn)O), which we don't even know the exact stoichiometry of. Should we start to put more focus on the other layers?

Susanne Siebentritt commented: Do we know enough about buffers as compared to absorbers?

I don't think we do – but it's very hard to characterise a thin buffer on top of a thick absorber. Growing the same thin film on another substrate is not very likely to give the same material, because we know there is a lot of interdiffusion between buffer and absorber. We need to develop new methods to learn, *e.g.*, about the doping of these thin films on top of thick (conductive) films.

Byungha Shin addressed Mohit Sood: From my experience with the coating of ALD ZnSnO onto CIGSe for PEC applications, I've learned that there was substantial migration of In from CIGSe to ZnSnO. We saw a strong In signal by XPS, even after the deposition of $\sim$20 nm ZnSnO, while other elements from CIGSe were not detected (as it should be, given the thickness of the ZnSnO overlayer). I am wondering if out-diffusion of In from CIGS also occurs during (Zn,Sn)O deposition in your case. This may explain why the longer deposition duration of (Zn,Sn)O led to a larger V_{oc}. Longer deposition duration could have led to a larger loss of In from CIGS, enlarging the band gap of the absorber and, thus, leading to a larger V_{oc}.

Mohit Sood answered: Thank you for your comment. While we did not explicitly check the out-diffusion of In in our samples, earlier studies with our ALD-deposited (Zn,Sn)O buffer do not show any out-diffusion of In in the Cu(In,Ga)Se_2 devices. Nonetheless, it is a nice suggestion and we will definitely look into it.

Rachel Woods-Robinson presented some information on a method to screen for tunability and alloys for PV: Computational "high-throughput" materials screenings for photovoltaic (PV) materials typically search for compounds within materials databases such as the Materials Project (MP),[1] the ICSD,[2] AFLOW,[3] and OQMD,[4] among others. For example, to look for PV absorbers, a database can be queried by a series of descriptors—band gap as a proxy for absorption edge within the visible wavelength regime; effective mass as a proxy for high mobility; and other metrics such as SLME[5] and various "defect tolerance" metrics[6]—to suggest a set of candidate materials for detailed experimental inquiry. This approach has been used successfully to propose new thin film PV absorbers, such as chalcogenide perovskites (*e.g.*, $BaZrS_3$ (ref. 7) and $LaYS_3$ (ref. 8)), pnictides (*e.g.*, $K_3Cu_3P_2$ and Na_2CuP (ref. 9)) mixed anions (*e.g.*, SbSeI (ref. 10)), among others,[11] as well as to propose new wide band gap carrier-selective contact or buffer materials such as BP and Ba_2BiTaO_6.[12]

However, these screening studies commonly only suggest stoichiometric, "pure" compounds, often those in which synthesis is difficult, doping is unsuccessful, or off-stoichiometry induces deviations from desired properties. In contrast, experimental progress typically starts from a well-studied, well-characterized material and, to achieve desired performance, properties are modified iteratively with the addition of dopants or alloying elements during growth. Most commercially-relevant thin film PV materials are alloyed or doped in this manner to access tunability, such as cadmium telluride ($CdSe_xTe_{1-x}$), III–Vs for space applications (*e.g.*, $In_xGa_{1-x}N_yAs_{1-y}$), CIGS ($CuIn_xGa_{1-x}S_ySe_{1-y}$), and more recently the kesterite family.[13] Thus, conventional PV material searches may exclude promising alloys in which tunable properties diverge from properties of their parent compounds. Given this discrepancy, a high-throughput framework to look for tunability in materials could be useful to enable the PV materials discovery community to explicitly search for alloys.

In Woods-Robinson, Horton, and Persson 2022,[14] a framework is introduced to systematically search for tunability in materials. For the first time, we create a database of tunable materials by connecting data in existing materials databases to suggest possible solid solutions between pairs of already-known materials. The resulting "alloy database" (here, "alloy" means a structurally commensurate pair of materials that may or may not be synthesizable) is publicly accessible such that researchers can perform their own queries and can filter outputs as they see appropriate. Thus, a new materials screening procedure is now possible that can be used to suggest new functional materials that may have been entirely overlooked by previous methods biased towards endpoint compounds.

Fig. 2 uses the known PV absorber Cu(In_xGa_{1-x})Se_2 to demonstrate how this alloy database is created and applied. "Alloy pairs" are constructed out of structurally commensurate endpoints, *e.g.*, $CuGaSe_2$ (mp-4840) and $CuInSe_2$ (mp-22811) deriving from the MP and ICSD databases (although in principle any database could be used). Next, "members" of alloy pairs are identified within the $CuIn_xGa_{1-x}Se_2$ tieline that structure-match to the endpoints within a given tolerance, such as $Cu_2InGaSe_4$ (mp-1224147). A "formula alloy pair" analysis can be performed as a proxy for stability to give a sense of whether or not it might be possible to synthesize a solid solution of a given polymorph across a given compositional tieline, and where a possible phase transformation may occur. Lastly, individual alloy pairs are connected into multinary "alloy systems", consisting of pairs that can in principle alloy with one another, such as $(Cu_{1-y}Ag_y)(In_xGa_{1-x})(S_zSe_{1-z})_2$ highlighted in bright yellow. This is just a subsystem; the full system for band gaps less than 3 eV is highlighted in light yellow (note, for the purposes of this demonstration, "band gap" refers to empirically-corrected band gaps calculated using DFT-PBE[15]). Using MP and ICSD to construct an alloy's database results in over 600 000 unique pairs, >11 000 alloy systems, >30 000 pairs containing members, and 19 000 formula alloy pairs.

Fig. 3 outlines a possible study that could be performed with this database to search for new earth-abundant PV absorber materials. The alloys database can be filtered to include only compounds with earth-abundant, non-toxic elements,

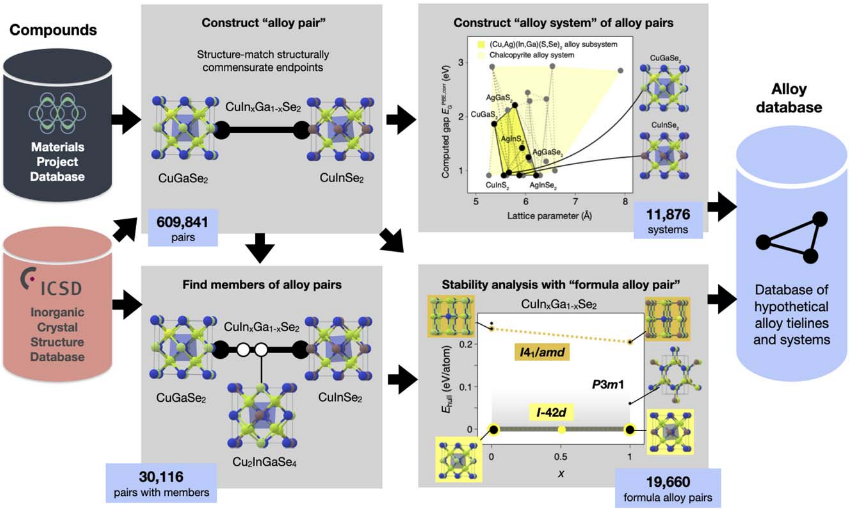

Fig. 2 Construction of the alloy database, using PV absorber Cu(In_xGa_{1-x})Se_2 as an example.

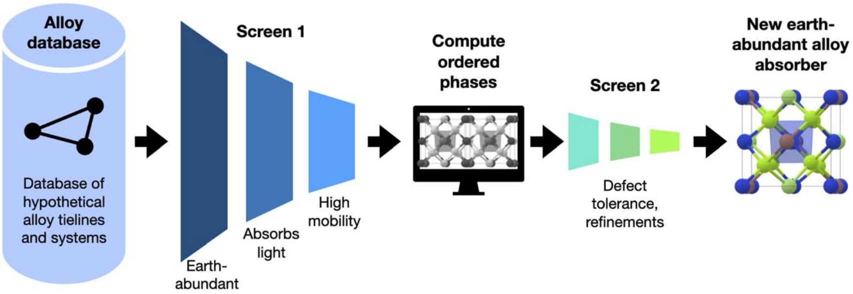

Fig. 3 An example screening for PV absorber materials using the alloy database.

then screened for alloy pairs band gaps suggesting absorption onset in the visible regime, and low electron and hole effective masses, for example. Then, alloy pairs can be filtered using the “formula alloy pair” stability formalism to generate a set of alloy pairs that may be of interest as PV absorbers. These are just preliminary screening filters; this method can be extended to other properties, and output tielines can be investigated to solid solubility and determine whether ordered (or disordered) phases might occur, using more in-depth modeling. As another example, in our paper we show an example of how this framework can also be applied to search for transparent contact layers for PV.

This method is intended as a tool to assist researchers as a starting point to explore tunability within existing databases. The framework is applied to MP and ICSD data, but in principle could be applied to any database of compounds with the open-source code we have made available. It is noted that no new calculations are performed here; rather, the method provides a new perspective into data that already exists. This work then enables new research, but users should be aware of its limitations; the alloys database is only as good as its underlying database. For example, errors in band gap due to the systematic underestimation of the DFT-PBE method will propagate from MP, and biases in structural diversity will propagate too (*e.g.*, oversampling of battery-related compounds, or of certain structure prototypes, *etc.*). It is also suggested to use caution when assuming Vegard’s law to interpolate properties; rather than an exact value, linear interpolation across a tieline gives a possible range of properties. To address these limitations, future work involves including non-commensurate alloy systems, completing “unmatched” tielines, computing ordered members, bowing, and estimating entropic contributions. Nevertheless, we hope this tool is of value to the community, and demonstrates the essentialness of considering tunability when performing materials discovery screenings.

1 A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder and K. A. Persson, *APL Mater.*, 2013, **1**(1), 011002.
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14 R. Woods-Robinson, M. K. Horton and K. A. Persson, *arXiv*, 2022, preprint, arXiv:2206.10715, **https://arxiv.org/abs/2206.10715**.
15 Á. Morales-García, R. Valero and F. Illas, *J. Phys. Chem. C*, 2017, **121**(34), 18862.

Nicolae Spalatu opened a general discussion of the paper by Seán R. Kavanagh: In your system you consider the Te interstitial and Cd vacancy as contributions to recombination; do you think the system is valid for as-deposited CdTe or after $CdCl_2$ treatment? In which case (CdTe as deposited or $CdCl_2$ treated CdTe films) is the concentration of the Te interstitial higher and why?

Seán R. Kavanagh answered: Our model focuses on as-deposited (intrinsic) CdTe, with the aim being to understand the intrinsic limiting factors for non-radiative recombination before extending our model to relevant extrinsic species (Cl, Se, As, Sb…). That said, the results remain relevant for $CdCl_2$-treated CdTe, as Te_i and V_{Cd} defects will still be present, however their concentration may be affected by the $CdCl_2$ treatment. For instance, V_{Cd} can form the A-centre complex with Cl_{Te},[1] though this is not a very strongly-bound complex[2] and so the concentration of 'free' V_{Cd} would not be expected to significantly reduce due to this complex formation. The potential diffusion of Cd into CdTe with the $CdCl_2$ treatment could, however, reduce the concentration of V_{Cd} by filling the vacant sites and removing the defects. For Te_i, again we expect no strong complex formation due to $CdCl_2$ treatment,[2] but the elevated temperatures and more Cd-rich environment during treatment will thermodynamically disfavour Te-related defects such as Te_i and Te_{Cd}, and so we would expect a decrease in the concentration of these species during $CdCl_2$ treatment, with an exponential dependence on the treatment temperature.

1 J. Pan, W. K. Metzger and S. Lany, *Phys. Rev. B.*, 2018, **98**, 054108.
2 D. Krasikov and I. Sankin, *J. Mater. Chem. A*, 2017, **5**, 3503.

Nicolae Spalatu asked: Is it possible to translate this model to emerging antimony selenide? What would be the possible metastable states?

Seán R. Kavanagh replied: As mentioned in our conclusions, anharmonicity, low symmetry and mixed ionic-covalent bonding are material properties that favour the existence of low energy metastable structures on the defect potential energy surface. Sb_2Se_3 and Sb_2S_3 exhibit each of these properties, and as expected we find many metastable defect structures in these materials, using our defect structure searching method.[1]

For instance, for V_{Sb}, a nearby Se atom moves to fill the void created by the vacancy, however this can be any one of the three inequivalent Se sites in Sb_2Se_3, each with slightly different energies and thus giving a ground state and two metastable structures for each V_{Sb}. These are detailed in ref. 1 and their effect on carrier capture will be described in future work from Xinwei Wang *et al.*

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1 I. Mosquera-Lois, S. R. Kavanagh, A. Walsh, D. O. Scanlon, *arXiv*, 2022, preprint, arXiv:2207.09862, **https://arxiv.org/abs/2207.09862**.

Jake W. Bowers asked: Following on from the importance of modelling chlorine in CdTe, are you planning on looking at adding Se to your simulations for CdSeTe? There is some experimental work showing that if both surfaces of the CdSeTe are passivated, you can get extremely long lifetimes (approaching microseconds). Is this something you will look in to?

Seán R. Kavanagh replied: Yes we are planning to soon publish our full in-depth analysis of all intrinsic defects in CdTe, before extending a similar level of analysis to relevant extrinsic species such as Se, Cl, As, Sb *etc.*

The recent developments with Se-graded CdTe solar cells are exciting for the community, but the mechanism behind the extremely long carrier lifetimes obtained in these materials seems little understood at this point. So this is certainly something we are keen to look into, and we hope to shed some light on the underlying mechanisms through explicit calculations of Se-related defects, as well as the effect of Se on the bulk properties such as the band-edges, dielectric screening, lattice deformation and effective masses.

Alex Ganose commented: How does this approach work in practice? Some materials will have very complex potential energy surfaces and there are an enormous number of potential metastable defect locations. What is the best way to find where they live?

Seán R. Kavanagh responded: Yes the prevalence of metastable configurations is a material-dependent phenomenon, depending on properties such as anharmonicity, combinatorial complexity, symmetry and bonding behaviour – briefly discussed in the paper conclusions (**https://doi.org/10.1039/d2fd00043a**). As such, materials which exhibit one or more of these properties could possess many metastable states, and this is particularly likely in the case of emerging inorganic solar materials such as Sb_2Se_3 and disordered compounds for example.

Tackling their identification is a very active area of development in the field of computational defect modelling, requiring structure searching techniques which can efficiently navigate the defect potential energy surfaces (PESs) and identify these local minima. Various approaches have been attempted, including random PES sampling, simulated annealing molecular dynamics, or ML-guided evolutionary algorithms. Recently we have proposed a method which demonstrates high performance (>95%) and good efficiency,[1] and so hopefully this and future developments will allow us to advance the accuracy and reliability of computational defect predictions; providing the full picture of potential defect configurations and thus impact on device performance.

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1 I. Mosquera-Lois, S. R. Kavanagh, A. Walsh, D. O. Scanlon, *arXiv*, 2022, preprint, arXiv:2207.09862, **https://arxiv.org/abs/2207.09862**.

Thomas P. Weiss asked: In the literature, several theoretical studies exist dealing with materials screening for photovoltaic (PV) applications. One of the criteria is that no deep defects should exist in the middle of the bandgap for a good PV material. However, this paper demonstrates that metastable defects can significantly contribute to recombination. Also, it seems that metastable defects exist in abundance, in particular for low symmetry crystal structures.

Therefor the question: to what degree can previous screening studies (without the consideration of metastable defects) be trusted when a particular (calculated) material does not indicate deep defects?

Seán R. Kavanagh replied: There are always *some* limitations with screening studies due to the requirement for coarse/empirical selection criteria in order to narrow the search space. While our work and other recent reports demonstrate that just because a set of *ground-state* defects do not present deep levels in the gap, this does not necessarily mean that defect-mediated non-radiative recombination will be slow, as metastable defects can provide alternative rapid carrier capture pathways. In this way, I think previous screening studies which predict materials showing a lack of deep defects (when ignoring metastable states) are decent indicators that those materials show some initial promise and may warrant further investigation, but cannot be trusted as reliable predictors of their actual recombination behaviour. This is an active area of development in the field of computational defect modelling, and our current methods of identifying these species are improving,[1] with the aim of greatly advancing the ability of *ab initio* techniques to accurately predict device performance.

1 I. Mosquera-Lois, S. R. Kavanagh, A. Walsh, D. O. Scanlon, *arXiv*, 2022, preprint, arXiv:2207.09862, https://arxiv.org/abs/2207.09862.

Rafael Jaramillo said: Which longstanding puzzles does this resolve? For instance, are there longstanding open questions regarding the interpretation of DLTS data that you can now resolve?

Seán R. Kavanagh answered: There are several longstanding puzzles regarding measured defect levels in CdTe – in fact this was one of our main motivations for applying these newly-developed theories to this material, to see if we can resolve some of these questions. One of the main difficulties in identifying defect levels in CdTe *via* DLTS or PICTS methods is the 'clustering' of deep levels in certain regions of the band gap. We find Te_i, Te_{Cd} and V_{Cd} all present defect levels in the 0.3–0.4 eV range above the VBM, in good agreement with experimental results. However, many of the experimental reports employ different sample preparation methods and show dispersion in the reported values, which in addition to the similar concentration dependence on growth conditions for these Te-rich defects makes their distinction very tricky. We find close agreement in terms of measured cross-sections, energy level position and concentrations with our calculations for Te_i, but would hesitate to make conclusions without the full context of all intrinsic defects present. We are performing this analysis now and hope to publish soon with a detailed comparison between the calculated and experimental recombination activity of defects in CdTe. Our work on V_{Cd} helped to clarify some of these issues, and a central point from this study is that the rulingout of certain defects as potential recombination sites based off their ground-state energetics may have been imprudent, as we show metastable effects can be key. We believe these results will help to obtain a more accurate picture of recombination-active defects in CdTe and clarify some longstanding controversies over the atomic origin of the measured levels.

Joachim Breternitz asked: The impact of these metastable defects is most likely not only defined by their thermodynamics, *i.e.* their energy of formation, but also by the kinetics, *i.e.* their rate of formation. Is this something that can be efficiently estimated?

Seán R. Kavanagh responded: Yes, absolutely the impact of metastable defects is dependent on both the thermodynamics (governing their formation and concentration under equilibrium conditions – *i.e.* 'in the dark') and kinetics (governing their rates of formation under operational conditions – *i.e.* 'under light'). Their kinetics can be efficiently estimated using modern computational approaches for mapping out potential energy surfaces such as the Nudged Elastic Band (NEB) method as used in our paper and shown in Fig. 4. From these, we can determine the energy barrier to the structural transition as well as the effective vibrational attempt frequency, and then estimate the transition kinetics using transition state theory. This transition rate then enters the final kinetic model of the recombination cycle. As discussed near the end of our paper, if this transition barrier is too large, the metastable defect will be kinetically-inhibited from impacting the recombination behaviour.

Thomas P. Weiss remarked: You looked at metastable transitions with a fast internal relaxation/excitation. However, did you also look at transitions with a large barrier in the configurational coordinate diagram? In Cu(In,Ga)Se_2, the V_{Se}–V_{Cu} defect complex can exist as a donor and as an acceptor.[1] Recently, we have shown that this transition is fast enough to occur during a current–voltage (*I*–*V*)

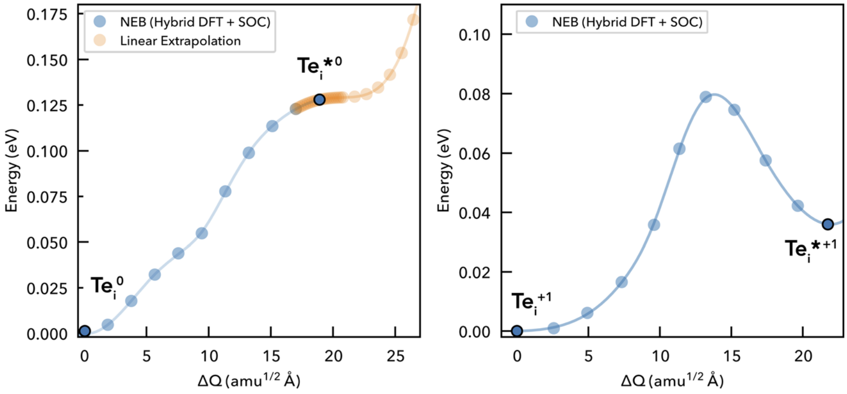


Fig. 4 Minimum energy paths along the potential energy surface between groundstate and metastable structures for (left) Te_i^0 and (right) Te_i^{+1}, calculated using the Nudged Elastic Band (NEB) method. Filled circles represent calculated data points and the solid line is a spline fit. X-axis given in units of mass-weighted displacement.

sweep and hence impacts the *I–V* characteristics. In particular, a higher diode factor is experienced, leading to lower fill factors.[2]

Therefore the question: do you see such metastable defects, which can change from an donor or acceptor (or *vice versa*) also in CdTe or possibly other materials?

1 S. Lany and A. Zunger, *J. Appl. Phys.*, 2006, **100**, 113725.
2 T. P. Weiss, F. Ehre, V. Serrano-Escalante, T. Wang and S. Siebentritt, *Sol. RRL*, 2021, **5**, 2100063.

Seán R. Kavanagh answered: Yes we have also looked at metastable defects which exhibit large energy barriers to the structural transition, and thus extremely slow internal relaxation/excitation. In our study of all intrinsic defects in CdTe, we identify several metastable structures for a variety of defects, using our defect structure searching method.[1] For some, the kinetic barrier to the structural transformation is low and thus they impact the recombination cycle, as in this work and previous work on V_{Cd},[2] but for several the transition barrier is quite large making these species inactive for recombination. Toward the end of our paper we discuss the range of energy barriers that will allow/prevent the metastable defect from impacting the recombination behaviour.

And yes, we do see such metastable defects which can change from a donor to an acceptor in CdTe, namely the Te-on-Cd antisite; Te_{Cd}. This will be discussed in our upcoming work, however, in this case a highly n-type (quasi-)Fermi level is required to transform to an acceptor, which is difficult to achieve experimentally due to compensating species.

We do see this in other materials, particularly those with anharmonicity, low symmetry and mixed ionic–covalent bonding which all favour the existence of low energy metastable defect structures, mentioned in the conclusions, as well as allowing amphoteric behaviour through the ability to distort, form new bonds and thus accommodate alternative charge states.[1]

For example, Sb_2Se_3 and Sb_2S_3 exhibit these properties and thus show many metastable defect configurations alongside amphoterism, as detailed in ref. 1 and will be discussed further in the context of solar cell performance in future work from Xinwei Wang *et al.*

1 I. Mosquera-Lois, S. R. Kavanagh, A. Walsh, D. O. Scanlon, *arXiv*, 2022, preprint, arXiv:2207.09862, **https://arxiv.org/abs/2207.09862**.
2 S. R. Kavanagh, A. Walsh and D. O. Scanlon, *ACS Energy Lett.*, 2021, **6**, 1392.

Christopher Savory asked: A conceptual question: given that you must already be working in a regime with shallow potential energy surfaces and potential anharmonicity where these metastable defect states are relevant, is there a concern about the reliability of the method in which we collapse all this information to a one-dimensional configurational coordinate? Should we be worrying about sampling a multiconfigurational space in this way?

Seán R. Kavanagh replied: Yes this is a concern. Calculating non-radiative recombination at defects is still very much an active area of research and method development. Current methods have shown good agreement with experiment and mostly consistent results across different approaches,[1–3] though each involves some approximations and thus has its own limitations.

An advantage of the 1D configuration coordinate model that we employ in this work, is that it does not assume harmonic potential energy surfaces (PESs) as in some of the other methods, and so one would imagine it is more robust for modelling carrier capture involving anharmonic PESs. That said, I think further work is needed to benchmark the accuracy of these methods for 'less well-behaved' defects as investigated in our work, and to tackle any deficiencies in the models that this might show.

1 L. Shi, K. Xu and L.-W. Wang, *Phys. Rev. B*, 2015, **91**, 205315.
2 L. Shi, K. Xu and L.-W. Wang, *Phys. Rev. B*, 2018, **97**, 077302.
3 D. Wickramaratne, J.-X. Shen, A. Alkauskas and C. G. Van de Walle, *Phys. Rev. B*, 2018, **97**, 077301.

Hasan Arif Yetkin opened a general discussion of the paper by Kostiantyn V. Sopiha: Yesterday we discussed the disorder which leads to band tails. How should we understand disorder in terms of the stoichiometry? *e.g.* Off-stoichiometry in a material is always thought of as a disorder!

Kostiantyn V. Sopiha replied: Our take is that the cationic disorder and off-stoichiometry are two distinct properties, which do not correlate but might nonetheless yield similar effects on the macroscale, including band tails.

Specifically, the cationic disorder is explained by the multiplicity of low-energy polytopes that can also be viewed as the incorporation of antisite domain boundaries in different quantities (typically the picture is simplified to swapping of cations, but the process is more complex as the system strives to maintain low deviation from the octet rule; see ref. 1). The resulting loss of long-range order and spatial inhomogeneities in the lattice at the nanometer scale lead to band edge perturbations associated with the band tails.

As we show in this work, the off-stoichiometry is incorporated into the lattice in the form of group-I-poor planar defects, which break the crystal symmetry and constitute spatial inhomogeneities with slightly different properties compared to the adjacent domains, most notably the valence band edge. The spatial perturbations in VBM and band gaps could be the source of band tails ascribed to the increased cationic disorder with respect to off-stoichiometry (without the actual cationic disorder being increased).

At the same time, our calculations suggest that there is no direct correlation between the off-stoichiometry and cationic disorder. The parameter we looked at is the above-hull enthalpy of polytopes with CuAu-type coordination, which stays roughly constant with respect to off-stoichiometry (these results will be published shortly).

1 J. K. Larsen, K. V. Sopiha, C. Persson, C. Platzer Björkman and M. Edoff, *Adv. Sci.*, 2022, **9**, 2200848.

David O. Scanlon asked: Its very interesting that you can now explain which materials show these OVCs. Do you know anything about their band edge alignments? How would these affect solar cell performance?

Kostiantyn V. Sopiha responded: We have not done the proper analysis of band alignments for these OVCs yet (constructing coherent interfaces, as suggested by ref.

1), but we can infer the behaviour from prior studies and the computed electronic properties (not shown in this work). We expect that the VBM position in OVC is progressively lowered with decreasing [I]/[III] ratio, while the CBM level is less affected. This assumption derives from the fact that the valance band edge in chalcopyrites is composed of antibonding I–VI states, removing which though lowering group-I content shifts the VBM downwards and thereby widens the band gap. Recently, the band alignment between 1 : 1 : 2 and 1 : 5 : 8 phases was computed for a wide family of I–III–VI systems, suggesting that the CBM is also shifted downwards with lowering [I]/[III] (see ref. 2). However, we note that, based on our calculations, the unstable OVC structures from earlier works have narrower band gaps compared to those of the stable structures identified in our study, meaning that the CBM lowering reported earlier is likely overestimated. Furthermore, unlike earlier works, we always observe the band gap widening with decreasing [I]/[III] ratio, meaning that the VBM shift downwards must be greater than the corresponding shift in the CBM (if any). The lower position of VBM and unaffected CBM in the Cu-poor Cu–In–Se has also been indirectly observed in our calculations (also not shown) in the layer-resolved DOS for $Cu_{10}In_{12}Se_{23}$. This change is consistent with the observed flattening of the VBM bands and the resulting enhancement of effective mass of holes moving across the Cu-poor region. We did not construct layer-resolved DOS for other I–III–VI yet, but we expect similar behaviour.

The impact of OVCs on the device is not completely clear at the moment, but it is probably dependent on the OVCs distribution, their composition, and the system in question. If we talk about a thin surface layer, as often assumed for CIGSe, it can have a mildly positive effect owing to the repulsion of holes away from the heterojunction due to the lower VBM of the OVC (see ref. 2 and references therein). On the other hand, if CBM forms a large cliff configuration, the impact can be detrimental due to the trapping of the electrons. If we talk about OVC precipitates through the absorber volume, which is more likely for systems with a large lattice mismatch between 1 : 1 : 2 and OVC phases (*e.g.* heavily Ag-alloyed CIGSe; see ref. 3), we suspect a negative impact as a result of transport barriers and/or dead absorber areas. In any case, we believe that the impact of OVC precipitates is not limited to the band offsets and must be analyzed in connection with, most importantly, the defect chemistry of both phases composing the mix.

1 S.-H. Wei and A. Zunger, *J. Appl. Phys.*, 1995, **78**(6), 3846.
2 A. Sharan, F. P. Sabino, A. Janotti, N. Gaillard, T. Ogitsu and J. B. Varley, *J. Appl. Phys.*, 2020, **127**, 065303.
3 J. Keller, L. Stolt, K. V. Sopiha, J. K. Larsen, L. Riekehr and M. Edoff, *Sol. RRL*, 2020, **4**, 2000508.

Susanne Siebentritt said: The hull curves seem to imply that the 1 : 1 : 2 compounds are not stable. They are higher in energy than the compounds with lower In or Ga. This means that the system could gain energy by splitting into the lower In or Ga compound and a Cu chalcogenide.

Kostiantyn V. Sopiha replied: No, the chalcopyrite 1 : 1 : 2 compounds are always stable. In fact, it is a terminal composition in my convex hulls, meaning that it cannot decompose into anything else represented in the figures. Although we have not done it, we are convinced that if we added group-I-chalcogenides to the convex hulls, the chalcopyrite 1 : 1 : 2 phases would have fallen on the convex hull (*i.e.* stable). Note that the negative formation enthalpies for ODCs in the-convex hulls, which you probably refer to, mean that these compounds are more stable than the MIXTURES of terminal 1 : 1 : 2 and 0 : 2 : 3 with the same compositions, but they say nothing about the stability of the terminal phases themselves. This is just how convex hull construction works.

Joachim Breternitz remarked: In the convex hull figures you show, for instance Fig. 1 in your paper (**https://doi.org/10.1039/d2fd00105e**), a number of the previously reported structures (which I assumed to be experimental?) are above the lowest energy form you report (and which would then not necessarily correspond to the experimental crystal structures at this composition). How far does this affect the overall conclusions you draw, when comparing the energies between the lowest possible states given they may not correspond to the experimentally observed ones?

Kostiantyn V. Sopiha responded: Thanks for your interest in our work. If I understood your question correctly, you are asking to what extent the errors in our DFT calculations (which you suspect from the experimentally observed structures being above the convex hulls presented in our work) may influence our conclusions. A short answer – not much, with the exception of a few less explored systems (primarily, with III = Al). To begin a long answer, a few things need to be clarified: (1) the “literature” structures include both experimental and previously reported DFT structures. (2) Structural isomorphs generated by isovalent replacements in the previously reported structures were also added as “literature” structures. (3) The “literature” structures also include ordered defect compounds, all of which were reproduced by our algorithm (but still labelled as “literature” , to give credit to the original works). Thus, one cannot judge from the presented convex hull about the possibly erroneous predictions of the ground states. However, we indeed observed a few of them, although for the 1 : 5 : 8 and 0 : 2 : 3 compositions only. For 1 : 5 : 8, we found two stable structural types – ODC-like and spinel. In one instance (*i.e.* the Ag–Al–S system), the experimental spinel phase was predicted to be above the hull. This case is already described in our manuscript and it could be explained by a variety of reasons, including (i) inaccuracy of the employed functional (we indeed found that the energy difference between these two structures changes considerably when PBEsol or SCAN functional is used instead of PBE), (ii) stabilization by the entropy contribution to the free energy, and (iii) experimental misidentification or our misinterpretation of the available experimental data. For the other systems, to our best knowledge, the predicted spinel ground states match experimental observations. For 0 : 2 : 3, a variety of symmetries were found experimentally in different I–III–VI systems. Some 0 : 2 : 3 compounds (*e.g.* In_2Se_3) are known to exhibit polymorphism. At this composition, we found that the predicted ground state is especially sensitive to the employed functional, *e.g.*, due to the ambiguities in capturing interactions in structures with a van der Waals gap. As a result, wrong ground states have been predicted for some binaries. Therefore, for the terminal 0 : 2 : 3 compositions, the predicted ground states and relative energies of different phases should not be trusted. It should be noted however that, based on the available experimental data, most I–III–VI systems considered (except for some with III = Al) form either ODC-like or spinel phases with (near-)1 : 5 : 8 composition.

This behaviour is reproduced computationally in the convex hulls. In these circumstances, the ground states and relative energies of the 0 : 2 : 3 phases do not affect the conclusion about the single-phase width because the crucial segment of the convex hull in the range $0.2 \leq [\mathrm{Cu}]/[\mathrm{In}] \leq 1$ is unchanged. In the case of the spinel 1 : 5 : 8 ground state, the width of the single-phase region can be affected if the magnitude of the enthalpy difference changes with the computational setup, as observed, but we find it highly unlikely that the predictions could be affected qualitatively.

Adair Nicolson asked: Since finishing the paper, have you gained any insights into why the I–Ga–S spinel is the only unstable sulfur spinel?

Kostiantyn V. Sopiha replied: We did not analyse this question in more detail after finishing the manuscript, so it is still a mystery to us. A part of the answer (explaining the instability of spinel in I–Ga–S *vs.* I–In–S) is to recall that the ratio of ionic radii, $R_{\mathrm{Ga}}/R_{\mathrm{S}}$, is below the critical value of 0.414 necessary for the stability of octahedral coordination (which is a part of the spinel structures). At the same time, the $R_{\mathrm{In}}/R_{\mathrm{S}}$ is above this threshold, making spinel structures stable in the sulfide systems with III = In. However, considering that Al is even smaller than Ga, the reason for the stability of spinel structures in I–Al–S must be different. It may potentially be related to the change in stability of the competing ODCs, but we have not done the analysis to verify this hypothesis.

Susan Schorr commented: In the Cu–In–S system the vacancy phase $CuIn_5S_8$, crystallizing in the spinel type structure, is formed. In this structure In is octahedrally coordinated by sulfur (as well as additionally some fraction of In is coordinated tetrahedrally by sulfur) (Fig. 5). To get an idea about possible coordinations, one can judge on the radio of r_K/r_A (r_K – cation radius, r_A – anion radius). There is a critical radii ratio for each coordination number which must not be undercut. The values are: coordination number 4 – 0.225, coordination

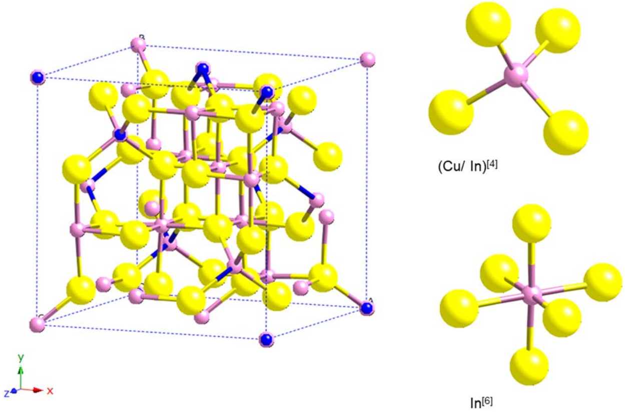


Fig. 5 Spinel-type structure of $CuIn_5S_8$, space group $F\bar{4}3m$ (blue - Cu, violet - In, yellow - S). On the right, the different coordination polyhedra of the crystal structure are shown: Cu and In are coordinated by 4 S forming a tetrahedron and in 6-fold coordination by S forming an octahedron. The numbers in brackets are the coordination numbers.

number 6 – 0.414, coordination number 8 – 0.732. This is basic textbook knowledge (*e.g.* ref. 1; I am sorry that I give a book in German here, but I use this for teaching the BSc students).

I would suggest that Ga^{3+}, which is much smaller than In^{3+}, does not fulfill this condition for a 6-fold coordination by sulfur.

1 W. Kleber, *Einführung in die Kristallographie*, 19th edn, Oldenburg Wissenschaftsverlag GmbH, 2010, p. 122.

Kostiantyn V. Sopiha replied: Thank you for the detailed comment. We agree with your explanation, but it does not answer the question, at least not fully. Adair asked why I–Ga–S are special compared to I–Al–S and I–In–S, reciting the discussion in our paper (see Fig. 5, **https://doi.org/10.1039/d2fd00105e**). The dependence on ionic radius was our first guess as well, but the considerations of critical ionic size ratios explain the stability of I–In–S *vs.* I–Ga–S only. The reason for the stability of spinel structures in I–III–S with smaller III = Al remains an open question to us. For reference, according to Shannon: for IV-coordinated ions; $R_{\mathrm{Al}} = 0.39$ Å, $R_{\mathrm{Ga}} = 0.47$ Å, $R_{\mathrm{In}} = 0.62$ Å for VI-coordinated ions; $R_{\mathrm{Al}} = 0.535$ Å, $R_{\mathrm{Ga}} = 0.62$ Å, $R_{\mathrm{In}} = 0.80$ Å, $R_{\mathrm{S}} = 1.84$ Å.

There are other, more complex structural factors (combining ionic radii and electronegativities) for spinel structures discussed in the literature.[1–3]

We have done a quick check, but no correlation between the computed energies and these factors was found. It might also be because the change in stability of the competing ODCs with respect to ionic ratios has not been accounted for. Though, frankly, we did not devote much effort to this question in our work because it falls a bit outside the scope, as written in the text. Incidentally, I think $CuIn_5S_8$ should not be called a vacancy phase, precisely because it has the spinel structure, which does not have any cationic vacancy sites (unlike zinc-blende-derived $CuIn_5Se_8$, which is indeed a vacancy phase).

1 K. Kugimiya and H. Steinfink, *Inorg. Chem.*, 1968, **7**, 1762.
2 M. G. Brik, A. Suchocki and A. Kamińska, *Inorg. Chem.*, 2014, **53**, 5088.
3 R. J. Hill, J. R. Craig and G. V. Gibbs, *Phys. Chem. Miner.*, 1979, **4**, 317.

Susan Schorr remarked: An accepted model for the formation of vacancy phases (I would not call them ordered vacancy phases because in our experimental studies on the crystal structure of vacancy phases we never found that the vacancies are ordered, see ref. 1 and 2) is the clustering of defect pairs (*e.g.* 2VCu + InCu in the case of $CuInSe_2$). Would your approach be complementary to that model?

1 S. Lehmann, D. Fuertes Marrón, M. León, R. Feyerherm, E. Dudzik, E. J. Friedrich, M. Tovar, Y. Tomm, C. Wolf, S. Schorr, T. Schedel-Niedrig, M. Ch. Lux-Steiner and J. M. Merino, *J. Appl. Phys.*, 2011, **109**, 013518.
2 S. Lehmann, D. Fuertes Marrón, M. Tovar, Y. Tomm, C. Wolf, S. Schorr, T. Schedel-Niedrig, E. Arushanov and M. C. Lux-Steiner, *Phys. Status Solidi A*, 2009, **206**(5), 1009.

Kostiantyn V. Sopiha responded: Our results prove that the model of clustering ($2V_{\mathrm{Cu}} + In_{\mathrm{Cu}}$) complexes is obsolete (although it can still be a useful simplification for some systems). To our knowledge, the view you mention (which is now dominant) has been developed in works by Zunger in the late 1990s (see ref. 1 and 2). The authors searched for the most stable arrangement of the complexes in $CuInSe_2$ and found that it corresponds to the stacking along [110] direction in the conventional cell. Based on this knowledge, a hitherto unknown, relatively stable structure of $CuIn_5Se_8$ was proposed (which has since become prototypical). As you can see, the notion of ODCs being formed *via* stacking of complexes was built into the original structural model BY DESIGN. However, it has serious shortcomings, one of which is that no stable structure of $CuIn_3Se_5$ and other compositions could be produced in this way. Instead, as a crude approximation, the properties of these ODCs were estimated as weighted averages of those for $CuInSe_2$ and $CuIn_5Se_8$.

In this work, we analyzed a lot more possible arrangements (limited only by the cell size and zinc-blende-derived symmetry), with the structures considered by Zunger being only a small subset. We found stable structures of $CuIn_3Se_5$, $Cu_2In_4Se_7$, and other ODCs, none of which could be formed by clustering of defect complexes. Moreover, for the $CuIn_5Se_8$ composition, a variety of structures more stable than the one discovered by Zunger (up to 2 meV per atom) were identified by our search, proving that defect complexes are NOT the building blocks of ODCs. From this conclusion it also follows that vacancies in the ODC structures are NOT V_{Cu} but simply empty cationic sides that are an integral part of the structure.

As an aside, I think the vacancy phases can indeed be called ordered, and it even follows from my interpretation of your findings. When you see vacancies predominantly on the 2a Wyckoff sites, it means that their distribution is not random. The vacancies are (at least partially) ordered, forming (001) planes with the spacing of $c/2$. This can also be interpreted as a change in crystal symmetry (to stannite-type + Cu/In disorder on 2b/4d), but I view it as a matter of representation. It is also worth remembering that fine structural features could have easily been missed out if a specific symmetry was imposed during the refinement of the diffraction data, and they could instead be ascribed to disordering. In this regard, it could be interesting to try refining the diffraction patterns with the structural models uncovered by our DFT calculation with the addition of partial disorder expected at finite temperatures.

On the other hand, I agree that the term "ordered defect compounds" is less appropriate as the vacancies are not defects in a classical sense (they are not formed by removing a specific species).

1 S. B. Zhang, S.-H. Wei and A. Zunger, *Phys. Rev. Lett.*, 1997, **78**, 4059.
2 S. B. Zhang, S.-H. Wei, A. Zunger and H. Katayama-Yoshida, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1998, **57**, 9642.

Susan Schorr commented: I would like to bring your attention to a number of experimental in-depth studies of the systems $Cu_2X–B_2X_3$ (with X = S, Se, B = In, Ga). The results of these studies would be a very good experimental complement to your very interesting theoretical work.

The papers I recommend to add are:[1–3]

1 C. Stephan, S. Schorr and H.-W. Schock, *Mater. Res. Soc. Symp. Proc.*, 2009, **1165**, 908.
2 C. Stephan, S. Schorr, H.-W. Schock and M. Tovar, *Appl. Phys. Lett.*, 2011, **98**, 091906.
3 C. Stephan, T. Scherb, C, Kaufmann, S. Schorr and H.-W. Schock, *Appl. Phys. Lett.*, 2012, **101**, 101907.
4 C. Stephan, D. Greiner, S. Schorr and C. A. Kaufmann, *J. Phys. Chem. Solids*, 2016, **98**, 309.

Kostiantyn V. Sopiha responded: Thanks for the recommendations. These works indeed provide an experimental perspective on Cu deficiency in CIGSe, but they are basically adopting the same point-defect picture as described in our introduction section. The estimations of homogeneity region width from publication no. 1 are also complementary to other works discussed in our article. Still, we recognise the potential of further model refinement through cross-verification with experiment, in which the results from the works you recommended could be pivotal. We plan such analysis after accounting for the partial cationic disorder (to reproduce experimental growth/treatment conditions), which is planned to be done using Monte-Carlo simulations in the future.

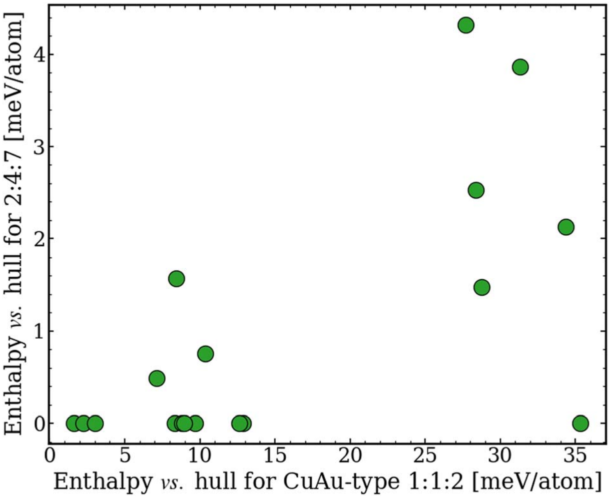
Rafael Jaramillo asked: Differential diffusivity can produce a photovoltaic effect. Would you expect a substantial PV effect due to differential diffusivity near these extended defects? If so, what are the voltage and length scales involved, and could these perhaps be measured? This could be a persistent yet hard-to-pin-down source of voltage loss.

Kostiantyn V. Sopiha responded: Great question. We think that Cu-poor planar defects could indeed be a source of voltage losses in CIGSe, but our explanation is somewhat different from the diffusivity difference. Specifically, considering that VBM in the Cu-poor regions is lower compared to the adjacent CIGSe domains, a hole concentration gradient (with hole depletion inside the Cu-poor planar defects) should be expected, which would yield a kind of local photovoltaic effect. The spatial extension of the gradient should not exceed the average separation between the planar defects, which is $\sim$6 nm for CIGSe with [Cu]/[III] $=$ 0.9. Hence, bearing in mind that the planar defect arrangement would lose out-of-plane periodicity and possibly form an intertwined 3D network at finite temperatures, the phenomenon we expect is more like potential fluctuations. Very roughly, the VBM variations can be estimated as the difference in band gaps of 1 : 1 : 2 and 1 : 5 : 8, which for Cu–In–Se is 0.3–0.4 eV. It is logical to assume that the magnitude of the resulting voltage perturbations is below that. However, we must admit that, for the planar defect with a thickness of only a few nanometers, band edges cannot be properly defined and should not be overinterpreted due to quantum effects. In addition, we expect that planar defects exhibit a very rich point defect chemistry distinct from that of the adjacent ideal CIGSe domains. Electrostatic potential perturbations and the resulting photovoltaic effect might emerge if the planar defects host charged point defect species, but it would take a dedicated study to evaluate its magnitude.

Experimental measurement for a single planar defect seems unfeasible, too, because they have not been detected in the first place yet. On the other hand, indirect signs could be analyzed by, for instance, measuring the absorber properties *vs.* [Cu]/[III] (*i.e.*, the concentration of planar defects). To this end, the knowledge that Cu-poor CIGSe generally exhibits better photovoltaic performance suggests that voltage losses do not increase with lowering [Cu]/[III], at least in the region of practical relevance. Thus, the planar defects seem to not induce large voltage losses. On the other hand, the planar defects might pose some benign properties that make Cu-poor CIGSe absorbers superior, and a combination of these effects is being observed experimentally. In any case, further research is needed to answer your question properly and in detail.

Seán R. Kavanagh said: In your convex hull results, there seems to be a correlation between the stability of ordered defect compounds (ODCs) and the thermodynamic accessibility of above-hull phases (*i.e.* many phases with energies only slightly higher than the hull when ODCs are stable), suggesting that atomic disorder is likely in these materials. Do think that the stability of ODCs at intermediate compositions is related to the propensity for structural disorder in these materials? What about other way around – do you think that if an emerging multinary material exhibits structural disorder, it is also likely to tolerate off-stoichiometry?

Kostiantyn V. Sopiha answered: That is an interesting question. The possibility of such a correlation sounds reasonable for the type-I and type-III systems (*i.e.* when a stable ODC is neighbouring the chalcopyrite phase in the phase diagram). The connection can be drawn *via* the disproportionality between the I–VI and III–VI bonds. From one side, the order–disorder transition temperature (for the ideal 1 : 1 : 2 stoichiometry) is known to correlate with the tetragonal distortion, which is determined by the difference in interactions along the *a* and *c* axes in the chalcopyrite unit cell (see ref. 1 and 2). From the other side, our results show that the lattice mismatch between the 1 : 5 : 8 ODC and 1 : 1 : 2 phases, which is also determined by the bond disproportionality, correlates with the enthalpy above the hull for the intermediate ODCs (and, thus, tolerance to off-stoichiometry for the type-I and type-III systems). Such a correlation is obviously absent for the type-II systems, as exemplified by the Cu–In–S system. However, when we plotted the above-hull enthalpy of 2 : 4 : 7 ODC (ignoring all non-ODC phases) against the above-hull energy of the CuAu-type structure of I–III–VI_2 (as a proxy for the order–disorder transition temperature; see ref. 3) for the entire family of 18 I–III–VI systems, we find little-to-no correlation (see graph shown here). Hence, it seems that the propensity for structural disorder and the tolerance to off-stoichiometry are not directly related, although they may indeed depend on combinations of the same structural parameters. I hope our future research can provide a clearer answer for chalcopyrites, but it is already clear that the correlation (if any) cannot be generalized for all emerging multinary materials.



1 J. J. M. Binsma, L. J. Giling and J. Bloem, *J. Cryst. Growth*, 1980, **50**, 429.
2 A. Zunger, *Appl. Phys. Lett.*, 1987, **50**, 164.
3 J. K. Larsen, K. V. Sopiha, C. Persson, C. Platzer Björkman and M. Edoff, *Adv. Sci.*, 2022, **9**, 2200848.

Cara Hawkins returned to the discussion of the information presented by Rachel Woods-Robinson and commented: As an experimentalist working on the design and discovery of new solar absorbing materials, this work is really exciting. I wondered if you might be able to talk a bit more about how this database will operate.

Rachel Woods-Robinson replied: The alloys database and framework can be accessed in three different ways. First is by the graphical interface on the Materials Project website (**https://materialsproject.org**; note, you may temporarily have to visit **https://next-gen.materialsproject.org** to ensure you see the latest features). Then you can go to the "materials detail page" of a specific crystalline compound, scroll down and view the alloy system that this material is part of, and filter that system based on a variety of parameters of interest. This will allow for basic searches. Second, the database can be accessed *via* the Materials Project's API using a Python interface, where you can query all the tielines and perform your own analysis (*e.g.*, construct your own "formula alloy pair"). This is typically done in a Jupyter notebook, and the website will have one-click links available to a pre-installed notebook for new users to try out the code without having to install anything on their own computer. Using the API will allow researchers to design more personalized searches. For example, in our paper[1] in order to screen for tielines of interest as p-type transparent top contacts for PV, we used the same API to filter for tielines in which PBE band gap and hole effective mass lie within a particular range of interest, and also screened based on the stability of all tielines between a given pair of chemical formulas (the "formula alloy pair"). This is an important point, because we want to emphasize that we generated the plots and analysis in the paper using the same publicly-available API that others will have access to, so these are fully reproducible. Third, all our code will soon be open source in the "pymatgen-analysis-alloys" package (**https://github.com/materialsproject/pymatgen-analysis-alloys**), so if you are interested you can add new functionalities or properties, add your own dataset as endpoints, or use the package to construct a new alloys database from a different compound database (*e.g.*, AFLOW[2] or OQMD[3]). We would be glad for others to get involved in the development and use of these tools, and welcome anybody is who is interested to contact us, regardless of previous experience.

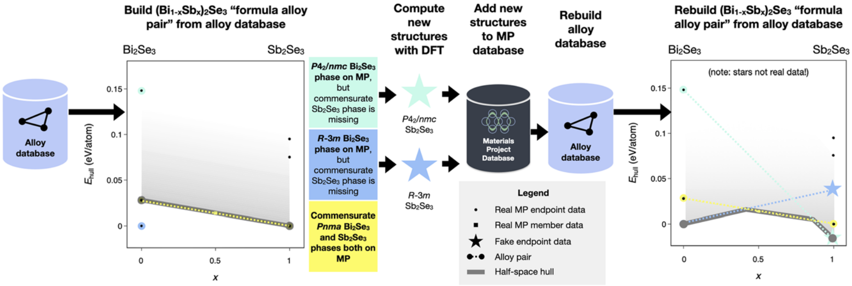
1 R. Woods-Robinson, M. K. Horton and K. A. Persson, *arXiv*, 2022, preprint, arXiv:2206.10715, **https://arxiv.org/abs/2206.10715**.
2 S. Curtarolo, W. Setyawan, S. Wang, J. Xue, K. Yang, R. H. Taylor, L. J. Nelson, G. L. W. Hart, S. Sanvito, M. Buongiorno-Nardelli, N. Mingo and O. Levy, *Comput. Mater. Sci.*, 2012, **58**, 227.
3 J. E. Saal, S. Kirklin, M. Aykol, B. Meredig and C. Wolverton, *JOM*, 2013, **65**(11), 1501.

Cara Hawkins asked: When will the database be available to use?

Rachel Woods-Robinson answered: In the very near future! MP has a small team of developers, and we currently are deploying a new website, but all steps are in place and ready for an initial deployment. We were waiting on the release of the preprint before doing so, but now that it has been done, the website functionality should also go live in its next deployment. A notice will be posted to our documentation page (https://docs.materialsproject.org/changes/website-changelog) when this goes live. Feel free to email me directly if you are interested in accessing the data before the release.

Joachim Breternitz remarked: Your zoom-background gives a great example of the structural variety that can be observed for seemingly similar compounds. I am always worried that computational approaches may miss lower energy crystal structures in a different structure, *i.e.* the stable structure of a multinary compound, because they have not been expected and not been accounted for. Is this something that can be effectively included in such calculations, or that would need to be included?

Rachel Woods-Robinson answered: The specific case of, say, a stable ternary alloy polymorph that is structurally incommensurate with both its binary endpoints would indeed be missed by our database as it stands today. The construction of our database is robust against small structural distortions and, indeed, it is not necessary for the alloy endpoints to necessarily be of the same spacegroup to be deemed close enough to be structurally commensurate (*e.g.*, consider a small polar distortion), although most are, but this will not catch all cases.



More broadly, this approach and high-throughput computational approaches in general may miss other experimentally-synthesizable materials. This oversampling of some structures and undersampling of others can be the result of biases such as which structures are present in nature, which structures are most common in technological applications (*e.g.*, zinc blende-derived structures for PV), which materials the database curators are most interested in, among other biases. Such "missing" structures in the alloy database can be divided mainly into two categories: (1) structures in which one endpoint compound exists in the underlying compound database (*e.g.* Materials Project) but a commensurate endpoint does not, and therefore an alloy pair tieline has not been constructed, and (2) structures that have yet to be identified in the compound database and therefore also do not appear in the alloy database (*i.e.* no endpoint compounds exist at all). There is also another case whereby (3) an alloy pair tieline may be discarded as "unstable" according to our enthalpy-based "formula alloy pair" analysis, but due to entropic effects it could actually be stabilized experimentally.

Towards the first case, part of the motivation of the "formula alloy pair" analysis is to demonstrate cases in which more data would be useful to add to the Materials Project database. For example, the left-hand side of the attached figure shows the formula alloy pair for PV absorber candidate $(Bi_{1-x}Sb_x)_2Se_3$ as constructed from the current version of the alloy database. MP has structures corresponding the *Pnma* phase for both endpoints Bi_2Se_3 and Sb_2Se_3, however the Bi_2Se_3 phases of $P4_2/nmc$ and $R\bar{3}m$ have no corresponding commensurate crystal structure for Sb_2Se_3, and so no alloy pair tieline for these phases can be constructed. Therefore, this analysis has identified "missing" data that can inform future calculations, which could then be added to the MP database and incorporated into a new iteration of the alloy database. As a result of the Materials Project infrastructure, this new alloy database will be automatically rebuilt as additional structures are added to MP. The right-hand side of the figure below also shows how the formula alloy pair plot could be reconstructed with the addition of new data (note: stars represent hypothetical data!), and how this new data could indeed change the computed stability across chemical space. One next step could be identifying similar scenarios with "missing" endpoints across all formula alloy pairs in our database, computing these structures, and then adding them to the MP database.

In terms of the second case – "missing" crystal structures that are not present in databases yet – there has been a lot of fantastic research into this space, ranging from data-mined ionic substitution to evolutionary algorithms, as well as new algorithms enabled by machine learning. The MP database has grown recently to include new crystallographic structures, and as new materials get added to compounds databases (from both case 1 and case 2), the alloys database can grow alongside.

The third case, in which experimentally synthesizable structures are missed computationally because they are not the lowest enthalpy structures, is also important.

Christopher Savory asked: Your database appears like it could be a powerful tool – though the stability of the mixed systems appears to be purely based on stability above hull. Are there any plans to introduce corrections on entropic terms, particularly configurational entropy, or will it remain based on ground state DFT total energies?

Rachel Woods-Robinson answered: The stability metric used in the alloys database is indeed just a crude estimate based on the enthalpy of both endpoints, so a more rigorous treatment including entropic contributions would make this a more useful and accurate tool. However, there is always a tradeoff with high-throughput methods in scale *versus* accuracy: we emphasize that the intended purpose of our tool is to help a scientist filter through a large set of potential alloys, and to use this to prioritize which ones would benefit from this more detailed treatment. Our alloy database includes >600 000 "alloy pair" tielines, each consisting of a unique chemical and structural space, and >19 000 "formula alloy pair" tielines, each consisting of a unique chemical space. It is noted that there are other hypothetical tielines not present yet in this alloy database because structurally commensurate endpoints do not yet exist in the underlying compound database; these are flagged (as mentioned in my previous reply), but without the corresponding endpoint present, no tieline can be drawn.

Scaling up entropy calculations to tens of thousands of tielines would be computationally exhaustive, but it might be possible to do this for hundreds of promising or interesting tielines, and this is our intent for future work. Obtaining reliable temperature-dependent phase diagrams for these tielines is our dream, but it is unclear how feasible this will be in a high-throughput context and, indeed, which approach to adopt. We are considering the Generalized Quasi-Chemical Approximation (GQCA)[1] but it is unclear if this will be accurate enough; a full cluster expansion might be better, but the ability to generate automated cluster expansions at scale is still in its infancy, and not something we are pursuing with this work. We welcome further input or collaboration on this topic and agree it is essential to address in the long term.

1 A. Sher, M. van Schilfgaarde, A.-B. Chen and William Chen, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1987, **36**, 4279.

Kostiantyn V. Sopiha said: Do you plan to include more complex systems, with co-alloying of several elements (*e.g.*, (FA,MA,Cs,Rb)PbI_3), on different sub-lattices (*e.g.*, (Cd,Zn)(S,O), (Ag,Cu)(In,Ga)$(S,Se)_2$), or with inclusion of vacancies (*e.g.*, solid solutions of $CuIn_5Se_8$–$CuInSe_2$ and CeO_2–Gd_2O_3)?

Rachel Woods-Robinson responded: Many complex alloy systems will fall out naturally from this method. Alloys are designed as “alloy pairs” first, and then complexity is built up by linking “alloy pairs” into “alloy systems” which defines co-alloying of multiple elements and sublattices. To the examples mentioned, (Cd,Zn)(S,O) would be an alloy subsystem of the larger wurtzite (or zinc blende, or other metastable polymorph) binary alloy system (*e.g.*, consisting of individual pairs CdS–ZnS, CdS–CdO, ZnS–ZnO), and (Ag,Cu)(In,Ga)$(S,Se)_2$ would be an alloy subsystem of the chalcopyrite ternary alloy system (see Fig. 2 for the latter example). A full alloy system can be filtered by cation, anion, and other properties such that a subsystem of interest can be represented; this could be performed for A = FA, MA, Cs, Rb, B = Pb, C = I for the example mentioned in the question; to date, we only support filtering by single atom ions on the web interface, but a user proficient in Python could filter by ions like FA, MA. Eventually, one can merge alloy systems such that binaries are connected to structurally commensurate ternaries (*e.g.* binary zincblende could merge with ternary chalcopyrite), which are then connected to quaternaries, *etc.* We are designing a platform such that these systems and subsystems can be easily queried by the user, and so that systems can be queried for properties of interest (*e.g.*, where in a given system could you alloy to find a band gap near 1.5 eV and lattice constant near 4 Å?).

The inclusion of vacancies and corresponding topotactic alloys could be an interesting addition to this method; we have considered the problem, though it is currently not part of the framework. Currently, the database requires sites to be occupied in order for two structures to be designated “commensurate”. Our code will soon be released and is open source, so this is something that an interested researcher could add!

Rachel Woods-Robinson returned to the paper by Seán R. Kavanagh and asked: Typically, DFT defect calculations assume thermodynamic equilibrium. However, light absorption and photocurrent extraction in solar cells occur under non-equilibrium conditions. Do you imagine the non-equilibrium defects that govern solar cell performance are not appropriately accounted for in our typical defect calculations for PV materials? Should we change the way we do defect calculations for PV?

Seán R. Kavanagh responded: Yes I believe this work and other recent reports in the field (*e.g.* work from Thomas Weiss,[1] our work on V_{Cd} (ref. 2) and other papers discussed in our introduction) show that metastable defects can play crucial roles in the e–h recombination process in semiconductors – particularly emerging ionic-covalent materials like Sb_2Se_3.

I believe non-equilibrium/metastable defects are not appropriately accounted for in our typical defect calculation workflow, stemming from (1) the difficulty in locating these structures in the first place, (2) the large computational cost of calculating non-radiative recombination behaviour, particularly for a range of defects at once and (3) our lack of understanding of their importance (aided by these difficulties in calculating them). Thankfully, these issues are diminishing each year with (1) improved algorithms for identifying these species (*e.g.* our defect structure searching method:[3] and this is a very active research direction at the moment), (2) exponentially growing computational power and efficiency and (3) increasing understanding of their importance as in this and other works.

So yes I think we need to change the way we do defect calculations, by expanding our search space to obtain the full picture of potential defect configurations (using structure searching methods such as ref. 3) and then determining all potential recombination pathways introduced by these states. In doing so, I believe we will dramatically enhance the accuracy of our predictions of solar cell performance and defect behaviour in general.

1 T. P. Weiss, F. Ehre, V. Serrano-Escalante, T. Wang and S. Siebentritt, *Sol. RRL*, 2021, **5**, 2100063.
2 S. R. Kavanagh, A. Walsh and D. O. Scanlon, *ACS Energy Lett.*, 2021, **6**, 1392.
3 I. Mosquera-Lois, S. R. Kavanagh, A. Walsh, D. O. Scanlon, *arXiv*, 2022, preprint, arXiv:2207.09862, **https://arxiv.org/abs/2207.09862**.

Jonathan J. S. Scragg opened a general discussion of the paper by Aron Walsh: I agree with the comments on defect tolerance. I want to remind everyone that "defect tolerance" only has meaning with respect to a material *property*. For example, it is meaningless to say that "material X is defect tolerant". But it is meaningful to say that *e.g.* carrier lifetime, PL intensity, conductivity, *etc.* in material X are defect tolerant. We need to be precise with this important term if it is not to lose its meaning altogether. In addition, let's think more of defect tolerance as being on a scale, rather than being a binary is/is not characteristic.

Alice Sheppard commented: From my experience of reading literature, we only see the publication of positive results and a lot of us could just be making the exact same mistakes as others previously. Should we encourage the publication of less successful results, rather than only if we see an improvement of device efficiency?

Aron Walsh answered: Yes, this should definitely be encouraged. Indeed, data from failed experiments is highly valuable for training machine learning models, which was recently demonstrated for the case of hydrothermal materials synthesis.[1]

1 P. Raccuglia, K. C. Elbert, P. D. F. Adler, C. Falk, M. B. Wenny, A. Mollo, M. Zeller, S. A. Friedler, J. Schrier and A. J. Norquist, *Nature*, 2016, **533**, 73.

David J. Fermin remarked: Following on the question by Alice Sheppard with regards to reporting ‘negative’ experimental results, are there ‘negative’ computational results? Are they usually published?

Aron Walsh responded: It becomes more difficult to define a negative result for materials modelling. There are cases where a lot of data is generated, for example in crystal structure prediction or property searches, that goes largely unused. But now even information on high-energy polymorphs or unphysical combinations of elements is valuable for training more robust statistical models. So computational researchers are encouraged to publish datasets that are as complete as possible.

Byungha Shin remarked: I agree with you on the importance of the dielectric constant of an absorber for screening of charged defects (as discussed in your paper **https://doi.org/10.1039/d2fd00135g**). We once believed that one of the reasons why kesterite wouldn’t perform as well as CIGS was because of lower dielectric constant of kesterite (which is 7–8) than that of CIGS (which is over 15). How sensitive is the defect tolerance to dielectric constant? For example, if there are two materials – one with dielectric constant of 5 and the other with 10, how much is the material with a dielectric constant of 10 better than the one with 5?

Aron Walsh responded: Thank you for raising this point. I fully agree and the lower dielectric constant for kesterite crystals is also found from first-principles calculations. When you look at the equations determining the interaction of electrons with charged defects, the dielectric constant appears in several places. In general the dependence is $1/\varepsilon^2$, for example in the Sommerfeld factor for carrier capture (see eqn (3) in ref. 1). So for the same defect concentration, a host material with $\varepsilon = 10$ would have a fourfold tolerance to carrier trapping compared to $\varepsilon = 5$.

1 S. Kim, J. S. Park, S. N. Hood and A. Walsh, Lone-pair effect on carrier capture in Cu_2ZnSnS_4 solar cells, *J. Mater. Chem. A*, 2019, **7**, 2686.

Joachim Breternitz said: I found your notion of low thermal conductivity very interesting. In a way, one could say that we might be looking for thermoelectric materials, too, which combine high electric conductivity with low thermal conductivity. Based on the work in thermoelectrics, it is evident that both cannot be tuned independently of each other but are related in some way. Do you believe that it may be possible to define a sweet-spot for solar cells, where the relation between thermal conductivity and electric conductivity is optimal – similar to the Shockley–Queisser limit?

Aron Walsh answered: Yes, there should be an optimal range for a given device architecture. This may be to slow hot carrier cooling or to reduce non-radiative recombination rates. I would like to see more detailed device models and numerical analysis on this topic in the future.

Jens Wenzel Andreasen commented: I have a collaboration with the spin-out company Lightnovo (**https://www.lightnovo.com**) who are developing several technologies based on Raman spectroscopy, including a microscope to map large areas in thin films with "2.5D" resolution. They are interested in PV materials with grain sizes upwards of 1 micrometer. Please contact me if you have for instance low-dimensional materials that could be suitable, and where there is an interest in mapping out crystalline phase distribution and orientations.

Conflicts of interest

There are no conflicts to declare.