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Novel chalcogenides, pnictides and defect-tolerant semiconductors: general discussion

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David O. Scanlon opened a discussion of the paper by Mirjana Dimitrievska: Thank you for the very nice talk Mirjana! Zn and P on their own are toxic and earth abundant, but when together as Zn_3P_2, they make a very potent rat poison. Are you worried by the toxicity of Zn_3P_2 as an absorber?

Mirjana Dimitrievska replied: This is a very interesting remark, that we actually hear quite often when we present our work on Zn_3P_2. While it is true that Zn_3P_2 is toxic when ingested (which is also the case for many other materials currently considered promising for PV), the layers that will be used in solar cells will be properly encapsulated, and should therefore not represent a danger to the environment. Additionally, Zn_3P_2 is also used as a fertiliser, and should therefore be recycled for this use after its end of life in solar cells. However, we still strongly advise you to not eat solar cells based on Zn_3P_2.

Jens Wenzel Andreasen commented: You report data that are stated to be grazing incidence X-ray diffraction, showing up to six diffraction orders, up to a 2-theta angle of about 50 degrees. This should not be possible for a monocrystalline film, as the crystal will be far off from Bragg conditions for the higher orders.

Mirjana Dimitrievska responded: Thank you for your remark. This was an initial mistake in the paper, which was corrected in the proofs. Indeed, the XRD measurements are done in the θ–2θ configuration.

Xinwei Wang said: In your paper (**https://doi.org/10.1039/d2fd00055e**), you mentioned that the defect concentration was much larger than the carrier concentration and you attributed that to the neutral defects, could it also be due to the compensation of positively and negatively charged defects?

Mirjana Dimitrievska replied: Thank you for your question. Yes, this indeed might be the case, as the calculated defect concentration based on the structural characterisation is of the order of 10^{21} cm^{-3}. This kind of estimation gives us a concentration of defects regardless of their charge. However, the reported charge carrier concentration for Zn_3P_2 is of the order of 10^{15} to 10^{16} cm^{-3}. This is why we think that some of the defects must be either neutral or charge compensated.

Matthew Sutton commented: Sb_2S_3 grown on orientated ZnO leads to no performance, while growth on randomly orientated ZnO leads to decent performance. This is due to the 1D Sb_2S_3 ribbons growing parallel to the substrate on the orientated ZnO giving poor charge transport. Zinc phosphide is not 1D, but do you think there could be a directionality effect at play, which is suppressed when amorphous?

Mirjana Dimitrievska answered: Thank you for your question. This is definitely something that needs to be investigated. But looking just from the crystal structure perspective, it would make sense that there is some anisotropy present, and that the orientation of crystals will play some role in the performance of the final device.

Rafael Jaramillo asked: Do you have PL comparing single crystal and polycrystalline films?

Mirjana Dimitrievska responded: Yes, we do have PL spectra from monocrystalline and polycrystalline samples, which have been published in ref. 1. In this reference you can see that there are two peaks present in the PL of the monocrystalline sample, at about 1.52 and 1.3 eV, while there is only one peak at about 1.37 eV which could be directly attributed to Zn_3P_2 in the polycrystalline sample. The other peaks in the PL spectra of the polycrystalline sample correspond to the InP substrate. We have studied in detail the PL peaks from the monocrystalline sample,[2] and we can attribute the peak at 1.52 eV to the band to band transition, while the peak at 1.3 eV is related to defects. On the other hand, the origin of the peak at 1.37 eV is not yet completely clear to us, and we plan to investigate this further.

1 M. Zamani, E. Stutz, S. Escobar, R. R. Zamani, R. Paul, J.-B. Leran, M. Dimitrievska and A. Fontcuberta i Morral, *J. Phys. Energy*, 2021, **3**, 034011.
2 E. Z. Stutz, M. Zamani, D. A. Damry, L. Buswell, R. Paul, S. Escobar Steinvall, J.-B. Leran, J. L. Boland, M. Dimitrievska and A. Fontcuberta i Morral, *Mater. Adv.*, 2022, **3**, 1295–1303.

Jonathan J. S. Scragg remarked: You mentioned that you had done DFT for your material (which you have made with a variety of off stoichiometric compositions). For which stoichiometry did you calculate?

Mirjana Dimitrievska replied: Thank you for your question. All our DFT calculations to date are done on perfectly stoichiometric Zn_3P_2. In the future, we plan to expand these calculations to take into account the off-stoichiometry conditions.

Byungha Shin asked: Have you checked the composition of single crystalline Zn_3P_2? Maybe the composition of Zn_3P_2 is different from the polycrystalline film? Single crystalline Zn_3P_2 is likely (very close to) stoichiometric and hence could be very insulating, which may explain why devices based on single crystals do not work.

Mirjana Dimitrievska responded: Thank you for your question. Indeed, we have produced both stoichiometric and very off-stoichiometric Zn_3P_2 monocrystalline samples as indicated in the paper (**https://doi.org/10.1039/d2fd00055e**). We have made solar cells out of all of them, and none showed any promising device characteristics. On the other hand, almost all polycrystalline samples showed good device characteristics regardless of the composition. We think that the main issue is not in the stoichiometry of the monocrystalline samples at the moment, but rather something else. It might be related to the device structure itself, or even the sharp interface that happens at the back of the films.

Kostiantyn V. Sopiha enquired: Do you think that the defects responsible for the off-stoichiometry are distributed randomly or form extended arrangements, similar to OVCs in CIGSe?

Mirjana Dimitrievska replied: Thank you for your question. Our current results from various characterisation methods (XRD, Raman and TEM) indicate that there is no ordering in the defects, and that they are randomly distributed throughout the structure.

Thomas P. Weiss said: In addition to steady-state photoluminescence spectra, do you have time-resolved photoluminescence curves? The extracted lifetime would give additional information about the material quality, as the steady-state photoluminescence flux can be equally improved/increased by increasing the doping density or the minority carrier lifetime.

Mirjana Dimitrievska answered: Thank you for your suggestion Thomas! Indeed, TRPL is something that we are working on at the moment, and will provide us with additional information on what is happening in our Zn_3P_2 films.

Thomas P. Weiss asked: Do you have an idea about the doping level in your phosphide films, as it has a strong impact on the photoluminescence flux? In other words: the higher the doping, the stronger the radiative recombination component.

Mirjana Dimitrievska responded: We are currently doing conductivity and Hall measurements in order to estimate the carrier concentration in our films. From the literature, it is estimated that the carrier concentration in intrinsic films with off-stoichiometric compositions is around 10^{15} to 10^{16} cm^{-3}. However, we do not know yet if that is the case in our films. What we do observe from the PL measurements, as shown in our paper (**https://doi.org/10.1039/d2fd00055e**), is that with an increase in defect concentration, the intensity of the defect-related PL peak increases, which signals higher recombination related to defects in general.

Thomas P. Weiss enquired: Did you ever grow epitaxial films with varying thickness?

Would you assume that the bulk quality remains the same?

From photoluminescence measurements on these films it would be possible to judge the surface recombination component.

In particular, if the epitaxial films have good carrier mobilities, the surface recombination lifetime can be very small.

Mirjana Dimitrievska replied: Thank you for your question. While we did grow epitaxial films with different thicknesses, we have not yet systematically looked at the effect of thickness on the optoelectronic properties. This is definitely something that we will do in the future, in order to determine the surface recombination component.

David O. Scanlon said: Have you considered doing DLTS to understand how many traps are present in Zn_3P_2?

Mirjana Dimitrievska answered: Yes, this is something that we are planning to do in the future. Thank you for the suggestion!

David O. Scanlon asked: Have you considered using positron annihilation spectroscopy to find the zinc vacancy in Zn_3P_2? For the phosphorous interstitial, you will likely need to rely upon theory, but for the zinc vacancy, positron annihilation could be very useful.

Mirjana Dimitrievska responded: Thank you for your suggestion, this is something that we will definitely implement in the future.

Nicolae Spalatu commented: A P-rich condition is required to have p-type conductivity. What would be the optimal/suitable treatment (temperature, partial pressure, time) conditions to achieve the optimal hole concentration?

Mirjana Dimitrievska replied: Thank you for the interesting remark. This is actually something that we are investigating currently, and hopefully we will be able to control the intrinsic doping concentration just with the deposition parameters.

Nicolae Spalatu asked: For such a system, do you have the phase diagram and partial pressure of the components depending on the temperature?

Mirjana Dimitrievska responded: Yes, the phase diagram of Zn_3P_2 is known, and published in ref. 1.

1 M. Ghasemi, E. Stutz, S. Escobar Steinvall, M. Zamani and A. Fontcuberta i Morral, *Materialia*, 2019, **6**, 100301.

Byungha Shin opened a discussion of the paper by Joachim Breternitz: In my experience with ZnSnN, the bandgap always increased with more oxygen impurities. In your ZnGeN, the bandgap shrinks up to 35% oxygen content (where the plot ends). Would the bandgap go up if more than 35% oxygen content was introduced?

Joachim Breternitz answered: This is an interesting question, which is hard to answer experimentally, simply because we never obtained such compounds. The value $x \approx 0.33$ corresponding to a composition of $Zn_{1.33}Ge_{0.67}(N_{0.67}O_{0.33})_2$ is the extreme we can reach experimentally, since we are starting from Zn_2GeO_4 with a Zn : Ge ratio of 2 : 1, which forms the upper limit for the Zn : Ge ratio in the oxide nitride – plus a small variation probably due to small Ge losses during the synthesis. If such materials would form, however, the bandgap would very likely go up again at a certain point since the oxide materials ZnO, GeO_2 and Zn_2GeO_4 as boundary compounds all have larger bandgaps than the oxide nitrides.

Rafael Jaramillo said: There have been papers in recent years (work of Roger Reeves, Steve Durbin, *etc.* – see for instance ref. 1) reporting systematic variation in the band gap with a point defect order parameter. To what extent do such correlations exist here, and what can we learn from this?

1 R. A. Makin, K. York, S. M. Durbin, N. Senabulya, J. Mathis, R. Clarke, N. Feldberg, P. Miska, C. M. Jones, Z. Deng, L. Williams, E. Kioupakis and R. J. Reeves, *Phys. Rev. Lett.*, 2019, **122**, 256403.

Joachim Breternitz replied: Thank you very much for this question. Indeed, there have been reports on variation of the band gap with cation order/disorder in several nitride materials, including $ZnGeN_2$ (see for instance ref. 1). The major complication in most experimental studies is that oxygen cannot be completely eliminated and it does play a role in the order/disorder mechanism as well as in the optoelectronic properties, as we show in our work (**https://doi.org/10.1039/d2fd00041e**). It must hence be taken into account in future work on such correlations. Furthermore, $ZnGeN_2$ has the disadvantage that Zn^{2+} and Ge^{4+} are isoelectronic and hence not reliably distinguishable from each other using X-ray diffraction. This prevents a similar analysis to that of Makin *et al.*[2] Therefore, other techniques such as neutron diffraction need to be used in order to disentangle the contributions from oxygen incorporation and cation disorder reliably. Our work on this is currently underway. Ideally, this would offer not only one, but two ways of influencing the band gap energy of these materials.

1 Q. Song, Y. Zhang, Y. Yang, Y. Xiao, T. Yin, L. Huang and H. Dong, *SSRN*, 2022, preprint, DOI: 10.2139/ssrn.4161327.

2 R. A. Makin, K. York, S. M. Durbin, N. Senabulya, J. Mathis, R. Clarke, N. Feldberg, P. Miska, C. M. Jones, Z. Deng, L. Williams, E. Kioupakis and R. J. Reeves, *Phys. Rev. Lett.*, 2019, **122**, 256403.

Elisabetta Arca asked: Have you experimentally measured the ionization potential – so have you experimentally measured that pushing up of the valence band because there is a large number of these zinc-based nitrides where we talk a lot about reduction or band gap opening, but there is very little experimental measurement of where the ionization potential is, and where the electron affinity is, and these are extremely important for device applications?

Joachim Breternitz answered: Thank you very much for this suggestion. We have not performed such measurements yet. However, this is a very important point that should be followed through in the future.

Mirjana Dimitrievska enquired: Regarding the O contamination in your materials, can this actually be used to tune some of the optoelectronic parameters? Can you perhaps control the concentration of O?

Joachim Breternitz responded: Thank you for this great question. Since oxygen inclusion in nitride systems is easily achievable, it may be a very fruitful strategy to use its incorporation for effective bandgap control, as a change of the optical bandgap with oxygen content is evident. We have analysed the chemical reaction for the formation of $Zn_{1+x}Ge_{1-x}(N_{1-x}O_x)_2$ in detail to understand the reaction mechanism and the synthesis conditions that are leading to defined compositions.[1] While our results so far concentrate on powders, an ammonolysis reaction on thin films would probably follow the same reaction mechanism and the parameters would only need to be modified accordingly.

[1] Z. Wang, D. Fritsch, S. Berendts, M. Lerch, J. Breternitz and S. Schorr, *Chem. Sci.*, 2021, **12**, 8493–8500.

Jonathan J. S. Scragg remarked: I liked the positive spin that you put on the presence of disorder, which was described as a mechanism for tuning material properties. Unfortunately, generally speaking, disorder is a problem rather than an opportunity. It adds non-periodicity, and what follows is band gap fluctuations on a variety of possible length scales. The existence of disorder seems inevitable when we derive "new" materials by isoelectronic substitution and we introduce multiple elements with similar radii. In the case of kesterites, we went from $CuInSe_2$ to $Cu_2ZnSnSe_4$, and we got Cu–Zn disorder. In your case, you went from a III–N to ZnGeN, and got Zn–Ge disorder. David B. Mitzi gave a different example (**https://doi.org/10.1039/d2fd00132b**), where the Zn in kesterite was replaced by a much larger atom, Ba. The structure was changed, but the disorder was eliminated. Are there some examples of new nitrides with very different cation sizes that might have similar properties to those you want, but that would lack disorder?

Joachim Breternitz answered: I am not sure the relationship between increasing disorder and increased problems for solar cells necessarily holds true. Some of the highest performing halide perovskite formulations actually contain multiple cations and yet preserve high efficiencies.[1] Therefore, the question may need to be viewed for every specific materials system.

The case of Cu_2BaSnS_4 is actually very different from kesterites, since the structure changes entirely. While every atom is tetrahedrally coordinated in kesterites, Ba^{2+} in Cu_2BaSnS_4 is 8-fold coordinated. This notable difference prevents disorder between this 8-fold coordinated Ba^{2+} position and the tetrahedrally coordinated positions of Cu^{+}. Such strong structural changes, however, also affect the electronic structure greatly, and direct assumptions about such compounds on the basis of the parent compounds are no longer viable. Such structural changes are observed in nitride materials, too. $SrZrN_2$, for instance, crystallises in a layered structure in an α-$NaFeO_2$-type crystal structure;[2] note that this crystal structure is very different from the β-$NaFeO_2$-type crystal structure observed for ordered $ZnGeN_2$, yet the same reservations for trying to rationalise properties on the basis of parent materials apply.

All cations are tetrahedrally coordinated in $ZnGeN_2$, which allows for disorder of the cations in this compound. The ionic radii (Zn^{2+}: 0.55 Å, Ge^{4+}: 0.39 Å (ref. 3)) are in fact considerably different from each other, and yet disorder is observed in these materials. The size difference between Zn^{2+} and Nb^{5+} (0.48 Å) in Zn_2NbN_3, for instance, is much smaller. It would probably be interesting to consider disorder in $ZnSiN_2$, where the size difference (Si^{4+}: 0.26 Å) is maximal, in order to testify whether size difference alone can prevent cation disorder in wurtzite-based nitrides.

1 C. Dong, Z.-K. Wang and L.-S. Liao, *Energy Technol.*, 2020, **8**, 1900804.
2 D. H. Gregory, M. G. Barker, P. P. Edwards and D. J. Siddons, *Inorg. Chem.*, 1996, **35**, 7608–7613.
3 R. D. Shannon, *Acta Cryst.*, 1976, **A32**, 751–767.

Jiwoo Lee commented: I work on Ge-based perovskites and tried to collaborate with experimental groups and they say it is hard to synthesise Ge thin films – do you know of successful cases?

Joachim Breternitz replied: The main difficulty with Ge-based halide perovskites is the fact that Ge is divalent in these compounds, *i.e.* as Ge^{2+}. However, Ge^{2+} is very unstable against oxidation into tetravalent Ge^{4+}, which is why Ge-based halide perovskites do form but are typically very unstable. In $Zn_{1+x}Ge_{1-x}(N_{1-x}O_x)_2$, on the other hand, Ge is always in the +IV oxidation state and hence such an instability due to oxidation would not be observed.

Nicolae Spalatu remarked: I have a question about the technological aspects of the experiments – what is the optimal annealing temperature? Is it done under pure oxygen ambient conditions or in the air?

Joachim Breternitz answered: In fact, the way we produce our bulk powder samples is through ammonolysis, *i.e.* reaction of the oxide materials under ammonia atmosphere at elevated temperatures. The dissociation of ammonia at higher temperatures leads to a reductive atmosphere that contains reactive nitrogen and hydrogen atoms, which on the one hand form the oxide nitride materials through nitrogen incorporation into the solid and on the other hand remove oxygen from the material through reaction with hydrogen to water. We have spent a considerable amount of effort establishing the relationship between composition and reaction conditions for the bulk materials[1] – which shows that relatively strongly reducing conditions lead to the formation of oxygen-poor films. I would anticipate that, while the exact conditions may be slightly different for thin films, such reducing conditions would also be needed for the ammonolysis of thin films.

[1] Z. Wang, D. Fritsch, S. Berendts, M. Lerch, J. Breternitz and S. Schorr, *Chem. Sci.*, 2021, **12**, 8493–8500.

David J. Fermin asked: Given that oxygen bonding is key for understanding changes in band gap with composition, would you consider doing EXAFS refinement of the O K-edge in order to validate the values reported in Fig. 3 of the paper (**https://doi.org/10.1039/d2fd00041e**)?

Joachim Breternitz responded: Thank you for this suggestion. In fact, Melamed *et al.* recently demonstrated the potential of O-XAFS for uncovering the disorder in such mixed anion systems[1] and it would be worth considering extending such studies to this system.

[1] C. L. Melamed, M. K. Miller, J. Cordell, L. Pucurimay, A. Livingood, R. R. Schnepf, J. Pan, K. N. Heinselman, F. D. Vila, A. Mis, D. Nordlund, B. Levy-Wendt, S. Lany, E. S. Toberer, S. T. Christensen and A. C. Tamboli, *Chem. Mater.*, 2022, **34**, 3910–3919.

Rafael Jaramillo addressed Joachim Breternitz and Susan Schorr: Following up on the point about the band gap *vs.* disorder – the model seems to be describing heterogeneous broadening on the atomic scale and local clusters where the chemistry is happening, rather than one extended solid. It comes back to the measurement, and what is meant by “band gap”. How do you define and measure the band gap?

Joachim Breternitz answered: This is an important question for materials with variable degrees of disorder. Our work is mainly based on space averaging methods: diffraction for the crystal structures as well as diffuse reflectance UV-VIS spectroscopy for the optical band gap. When we refer to band gap from an experimental point-of-view, we refer to the optical band gap determined with the said method. Therefore, very small inhomogeneities may be challenging to spot, if they are evenly and randomly distributed. However, there is no indication from X-ray diffraction that would signify small coherent scattering domains – which would result from such inhomogeneities – and which would be expressed in strong peak broadening. Therefore, I would assume that the composition and crystal structure are largely homogeneous throughout the tested material without a smoking gun for separation.

Kostiantyn V. Sopiha commented: If not done already, it might be worth checking the stability of your oxynitride structures with respect to all competing phases (from DFT). Segregation of oxides (forming a mixture of oxide and nitride phases) could be more energetically favourable than the oxynitride phase.

Joachim Breternitz responded: This is an interesting suggestion, thank you very much. From an experimental point-of-view, we have never observed such a decomposition having studied the materials with space averaging techniques, such as powder diffraction and diffuse reflectance UV-VIS spectroscopy. In fact, oxide nitride materials are well researched solid-state materials without a particular trend for segregation, as far as I am aware.

Elisabetta Arca said: We have worked quite a lot on this type of zinc-based nitrides and we never saw segregation and we have done extensive TEM and EDX-coupled microscopy, so I don't think you will have segregation based on the result of another lab on the same material system – we don't see them.

David O. Scanlon asked: Is disorder always bad? It seems that certain types of disorder have been shown to improve material performance for example in $AgBiS_2$ devices, so perhaps we need to think about how we discuss the role of disorder?

Seán R. Kavanagh answered: I agree. I think the classification of disorder as always bad is too black and white, and is inaccurate in many cases, exemplified by recent work on cation-disordered chalcogenides (*e.g.* $AgBiS_2$[1]) and mixed-cation mixed-anion perovskites[2] as noted by Kostiantyn.

Whether disorder has a positive or negative effect on properties and performance seems to be a material-specific question, depending on the underlying bonding interactions and how disorder affects this. For instance, in the cation-disordered nitrides, kesterites and $NaBiS_2$ where we have site-swapping of heterovalent species, we see the formation of localised chalcogen *p* states above the VBM, which act as fast carrier traps and kill performance – as mentioned by Kostiantyn. This behaviour seems to be avoided in the mixed-cation mixed-anion perovskites (exhibiting homovalent disorder), but also to some extent in $AgBiS_2$ however, suggesting certain materials may exhibit a 'disorder tolerance', in which disorder could be a useful parameter to tune and optimise performance, but will harm performance in 'disorder intolerant' materials.

1 Y. Wang, S. R. Kavanagh, I. Burgués-Ceballos, A. Walsh, D. O. Scanlon and G. Konstantatos, *Nat. Photonics*, 2022, **16**, 235.

2 K. Frohna, M. Anaya, S. Macpherson, J. Sung, T. A. S. Doherty, Y.-H. Chiang, A. J. Winchester, K. W. P. Orr, J. E. Parker, P. D. Quinn, K. M. Dani, A. Rao and S. D. Stranks, *Nat. Nanotechnol.*, 2022, **17**, 190–196.

Kostiantyn V. Sopiha replied: It should be noted that CIGSe is disordered (In and Ga share the same sub-lattice). Halide perovskites are also disordered on different sublattices but perform well as solar absorbers nonetheless. These are good examples showing that disorder is not inherently detrimental. I think it is all material-specific. If complete randomness of site occupancies occurs between isovalent elements on the same sublattice, I see no reason why it should be harmful. The issues may arise when electrostatic potential perturbation emerges due to disorder, which can occur when ions with different valences are swapped.

Elisabetta Arca commented: Following up on David's question and as more of a comment, in this zinc compound, it seems to be bad, because band gap narrowing or opening is indicative of band edges moving and that is never good because it's probably tail states, and in fact the actual performance of the solar cell is pretty poor. If we talk about other material systems that are more defect tolerant, that's a different issue, but for this one it's never good.

Aron Walsh remarked: Jonathan J. S. Scragg raised a point querying examples where disorder has been beneficial. I would argue that alloys, for example (S,Se) as used in chalcopyrite and kesterite technologies, are one substantial example. The mixing of A-sites in perovskites would be another where homogeneous mixing provides tunability. However, I do recognise that these cases are distinct from site disorder in a stoichiometric crystal.

Jonathan J. S. Scragg answered: Agreed, but if disorder is defined as a deviation from periodicity in the lattice, most alloys will be inherently disordered (presumably perfectly periodic arrangements of S or Se would be possible, but they are not likely). Thus alloying inescapably introduces disorder, but it is not the disorder itself that is beneficial. If it were possible to separate these effects, it might still be found that the disorder is detrimental in terms of having a contribution to band tails, lower mobility, *etc.*

Jonathan J. S. Scragg asked: Can the influence of disorder be decoupled from the effects of alloying? Will an alloy always bring with it some degree of band tailing, because of the lack of perfect periodicity?

Aron Walsh responded: This is an excellent question which would require some deep thinking to answer fully. I feel that you are correct in stating that some degree of band tailing is unavoidable. Even for a regular homogeneous solid-solution, the distribution of chemical environments will give rise to spatial fluctuations in the electronic structure.

Rachel Woods-Robinson remarked: One question that has continued to emerge in this discussion is whether "disorder is bad for PV materials". As other participants have mentioned, the effects of disorder are very material-specific. A rule-of-thumb like this was likely developed with a few well-studied materials in mind (*e.g.* CZTS), and therefore should be used with caution especially when studying new materials.

An additional point is that usually the phrase "PV materials" is interpreted to refer to absorbers, since they are the most heavily studied, however it is important to clarify that "PV materials" also include contacts, buffer layers, light-trapping layers, *etc.*

Disorder is indeed often very useful to attain useful properties in contact materials or buffer layers. For example, some of the best n-type transparent conductors are amorphous or highly disordered.[1,2] Another example is that in materials where conduction is dominated by polaron hopping, such as $NiCo_2O_4$ spinels which have been proposed as transparent contact layers in photoelectrochemical cells, disorder has been shown to reduce the hopping barrier and actually lead to increased conductivity.[3] Therefore, whether disorder correlates with increased or decreased PV performance depends on the application, the specific material and its physics, and the type of disorder.

1 A. Walsh, J. L. F. Da Silva and S.-H. Wei, *Chem. Mater.*, 2009, **21**(21), 5119–5124.
2 D. S. Ginley and J. D. Perkins, *Handbook of transparent conductors*, Springer, Boston, MA, 2011, pp. 1–25.
3 G. J. Exarhos, C. F. Windisch Jr., K. F. Ferris and R. R. Owings, *Appl. Phys. A: Mater. Sci. Process.*, 2007, **89**(1), 9–18.

Aron Walsh addressed Joachim Breternitz: Traditionally, metal pnictides would have been overlooked for emerging PV applications due to the requirement for expensive growth techniques that avoid oxygen contamination. In most scalable fabrication approaches oxygen is unavoidable. Is this something that we can live with for this new generation of materials?

Joachim Breternitz replied: It is certainly true that oxygen incorporation is traditionally considered unavoidable in the synthesis of nitrides in particular. This is due to the reaction inertness of N_2 as opposed to O_2,[1] which means that at the highly energetic reaction conditions necessary for nitrogen activation (through temperature/plasma *etc.*), any traces of oxygen or water would react preferentially. Zakutayev *et al.* argue that the paradigm of pricey syntheses due to expensive techniques may be overcome through the combination of synthesis and theoretical calculations, which allow much more targeted synthesis efforts.[2]

The experimental evidence for the impact of oxygen for solar cell devices needs to be established reliably, before a convincing conclusion should be drawn as to whether oxygen is killing performance. I would not feel confident assessing at this stage, whether oxygen really has such a detrimental effect, or whether a device would be able to perform well with oxygen incorporation. Oxygen clearly has an effect on the bandgap of the material, and hence if it is unavoidable during the synthesis, it needs to be taken into account at the point of materials characterisation and understanding and may even offer an effective way to tune the materials properties.

1 W. Sun, A. Holder, B. Orvañanos, E. Arca, A. Zakutayev, S. Lany and G. Ceder, *Chem. Mater.*, 2017, **29**, 6936–6946.
2 A. Zakutayev, S. R. Bauers and S. Lany, *Chem. Mater.*, 2022, **34**, 1418–1438.

Rachel Woods-Robinson addressed Mirjana Dimitrievska: It has been reported that under some polarization conditions Zn_3P_2 has a dipole forbidden optical transition at or near the direct gap, such that the VBM to CBM transition is not allowed or very weak.[1–3] Has this been confirmed computationally or observed experimentally in your work? If this is indeed the case, do you expect that the existence of a weak band-edge transition may be a problem for how viable Zn_3P_2 is as a PV absorber?

1 V. J. Rao, M. V. Salvi, V. Samuel and A. P. B. Sinha, *J. Mater. Sci.*, 1985, **20**(9), 3277–3282.
2 J. Misiewicz, *J. Phys.: Condens. Matter*, 1990, **2**(8), 2053.
3 D. M. Stepanchikov and G. P. Chuiko, *Condens. Matter Phys.*, 2009, **12**(2), 239–248.

Mirjana Dimitrievska answered: Our recent computational and experimental analysis on the band structure of Zn_3P_2 nanowires, ref. 1, shows only the presence of a direct bandgap. This has been proven using two techniques, ellipsometry and VEELS measurements. To date, we have not seen experimental proof of the presence of the forbidden gap. In general, the forbidden bandgap might not be so detrimental to solar cell performance. For example, Si has a forbidden bandgap of 1.1 eV, and it still works for PV.

1 M. Dimitrievska, F. S. Hage, S. Escobar Steinvall, A. P. Litvinchuk, E. Z. Stutz, Q. M. Ramasse and A. Fontcuberta i Morral, *Adv. Funct. Mater.*, 2021, **31**, 2105426.

Jens Wenzel Andreasen opened a discussion of the paper by Thomas Unold: You stated that 80% of data are lost after 2 years. I am curious as to whether you, or anybody else, have any idea what the amount of usable data is? We all know that some experiments fail for some reason, poor design or unavoidable artifacts. Is it desirable to report all data and make them FAIR? Some fraction might be "garbage" data. Do you have some idea as to what the realistic fraction of usable data is, and how far we are from reaching a reasonable degree of FAIR for this fraction?

Thomas Unold replied: I can only speak from my labs and labs I have worked in – I would say that from there at least 90% of the data would be usable, if they are decorated properly with metadata.

Jens Wenzel Andreasen said: A follow up question: would it be an idea to have a metadata field/category stating something like "garbage data, use at your own peril", perhaps with an explanation of the shortcomings, so that such data is not fully lost?

Thomas Unold responded: I do not know what you mean by garbage data, but from the way it sounds, this is of course not data you need to report. What I refer to is sound data which are not used in publications, or even data which have been in some way or another used in publications. Typically all of these data are lost to the community. My group has many data that have not been published, maybe not understood by us, but other groups or scientists could possibly use and interpret them – I certainly would not classify them as garbage data

Joachim Breternitz commented: It is important to make the distinction between incorrect data, which may arise from a technical mistake, for instance, and data that is technically sound but may not appear useful in the very situation it was acquired. A database could, and probably should, contain the latter and it is hence important to make that distinction.

Prakriti Kayastha remarked: I feel very strongly about sharing data freely. Sometimes it is not clear how to reproduce a calculation/procedure described in a publication. I think it is important to share all relevant information to reproduce it. As a PhD student, sometimes one ends up running the same calculation someone has run before. To avoid this, it is useful if raw data is made freely available alongside the publication.

I do understand that collecting raw data can seem unnecessary, but it can be extremely useful to the larger community and I feel the push can come from the publisher's/editor's end during publication.

David B. Mitzi commented: In terms of providing a uniform format for registering machine-actionable data related to solar cell performance and/or optoelectronic properties, the field of crystallography has the cif file and associated cifcheck applications for assessing the completeness and quality of the associated data, which might serve as a useful model. An important aspect of this approach is, not just the uniform data format, but also associated automated tools for assessing the quality of the data, which for example must be used and the problems addressed when results are reported in the literature.

Thomas Unold answered: The cif format is indeed a good model example of how this could work. I was not aware of the cifcheck before – to provide such tools to check the integrity of measurements/data would be very useful. For example, I could see the need for such tools for composition determination. With respect to *JV* there are a number of checks that could be performed.

Susanne Siebentritt stated: This is an appeal to everyone: when you publish solar cell data, do not only present j_{SC}, V_{OC} and FF, but the full *jV* curve – and make it available in digital form, *e.g.* as an ascii file *e.g.* on **https://zenodo.org**.

Zenodo is a FAIR platform, is run by CERN and is guaranteed to exist as long as the European Union exists.

The appeal to provide digital data applies to all measurements (at least those you show in the paper). It would be great to also provide digital EQE data for all solar cells (absolute EQE, not normalised). We've all tried to digitise data from graphs in papers, which just adds errors.

This is also an appeal to the editors (I'm putting forward here an idea from Jonathan J. S. Scragg): you could just demand for each graph the ascii data and provide it with a link on the graph.

Susanne Siebentritt commented: There are already several databases: Materials Project, NOMAD, *etc.*

Everybody has their pet database and some people promote their own database.

Do you have an idea of how to get people to agree on a joint database?

Thomas Unold responded: I think a joint database would have to be open-access (no fees) and with functionalities that are convincing. This is similar to the question of why most people started to use Google as a search engine, although I am not suggesting there should be collection of metadata on the users and advertising.

Joachim Breternitz remarked: You mentioned cif files, which are a successful case that can serve as a model for the development of a unified format for solar cell data. Still, it is important to remember that developing this ostensibly simple format has taken about 30 years and is still continuously developed under the lead of the International Union for Crystallography (IUCr). Therefore, we need to be aware that such a task is a huge effort and cannot be solved in a short time by a limited number of researchers, especially since the complexity of a format for solar cells will arguably be even higher for solar cells as compared to crystallographic data.

Alex Ganose commented: Creating a single computational materials database is big challenge – particularly because different databases have different objectives, *e.g.*, some are focussed on curated data and others on collating experiments from multiple researchers. However, there has recently been progress on a standardised way of downloading and querying many of the most popular computational materials databases, such as the Materials Project, AFLOW, Crystallography Open Database (COD), Joint Automated Repository for Various Integrated Simulations (JARVIS), Materials Cloud, Materials Platform for Data Science (MPDS), NOMAD, and the Open Quantum Materials Database (OQMD). This has been made possible through the OPTIMADE query specification (**https://www.optimade.org/**). This means with the same query you can download all matching data from any data provider that supports the specification.

Marcus Bär asked: Is there an initiative (*e.g.* within the PV community) to agree on common data formats, metadata categories, *etc.* to realize this 'dream' of FAIR data?

Thomas Unold replied: In fact there is a lot of development in this field right now, we are currently starting the discussion about data formats, metadata categories and ontology developments in several national as well as European projects. As far as I know there will also be some decisions later this year about standards for FAIR digital objects, see the GO FAIR Initiative (**https://www.go-fair.org**).

David O. Scanlon said: We computational chemists have a number of databases we can access, and each one has its own issues/errors. PV is a very wide community, and people employ so many different techniques to interrogate their materials. How do you standardise all the distinct data formats for all the different types of techniques that provide insight into material/device performance? Would we need to ask the communities developing/using each technique to agree on a format, and then come back to the PV community with their conclusions? How do we pull it all together to ensure the data can be FAIR?

Thomas Unold answered: I think work on some sort of standardization would make sense, and alternatively or additionally, working on an ontology where the measurements, quantities and units are defined. In this way different data formats can be used, but the data will be easily readable by everyone.

Some sort of universal metadata header in files would probably make sense, similar to what we have in images and pdfs. There the type of data, format and units could be defined, so that a computer can immediately read the file.

Rafael Jaramillo asked: Do we have any outstanding proof-of-principles wherein uploaded experimental data was retrieved and analyzed by a 3rd party, and then used to make a significant discovery or save a substantial amount of time? Perhaps these examples abound in industry?

Thomas Unold replied: A good example of what can be done is presented in a recent article in Nature.[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.

Mirjana Dimitrievska enquired: While building databases is important, how important is it to also trust the data in the database, that it has been measured correctly for example?

Thomas Unold responded: I think it is important to be able to judge the validity of data in a database. This will become easier when the size of databases increases and there are multiple measurements by multiple groups. A system for curation and rating of results will be needed. To check or judge whether a measurement was performed correctly, rich metadata about the measurement process will help.

Jake W. Bowers commented: When talking about how to make sure data is ‘good’, there is already the International Organization for Standardization, who make standards for all types of measurement. There are already standards available, for example on how to measure *IV* curves properly, and how to measure an EQE curve taking into account mismatches between the device under testing and the reference. These standards are formed by a committee of international experts, and so the framework to facilitate making these protocols to get ‘good’ data is already there. We just need to make use of it for other measurement types.

Susan Schorr opened a discussion of the paper by Matthew Smiles: In your talk the indexation of the Bragg peaks in the figure of the XRD pattern was not correct. In the corresponding figure in the paper (Fig. 5, **https://doi.org/10.1039/d2fd00048b**), the indexation of the Bragg peaks is correct.

Phillip J. Dale remarked: Tin selenide can be formed as SnSe or $SnSe_2$. In your germanium selenide films do you see just GeSe or do you also get $GeSe_2$? It will depend on the vapour pressure of selenium.

Matthew Smiles replied: We have completed Raman, XRD, and photoemission which show no evidence of forming $GeSe_2$. In comparison, GeS photoemission shows evidence that GeS_2 forms on the surface.

Nicolae Spalatu asked: Did you try to perform the treatment in Se-rich conditions?

Matthew Smiles answered: No attempt was made to try the material in a Se rich environment.

Mohit Sood commented: You report capacitance–voltage measurements in your work, can you please comment on the frequency at which these measurements were made?

Matthew Smiles replied: Measurements were made using a 1 MHz AC frequency.

Mohit Sood asked: How did you decide which frequency to use for capacitance–voltage measurements?

Matthew Smiles responded: Measurements were made using a deep level transient spectroscopy system which has a fixed frequency for analysis.

Mohit Sood remarked: We observe that the solar cells have a rather low shunt, however, when observing the $1/C_2$ *vs.* voltage plot, I don't see a drop in voltage. Is it the actual voltage across the junction that you plot there or the applied voltage? If the V is not the actual voltage across the junction then in your work the $1/C_2$ *vs.* V plot should be very different. And I suspect the doping values will also be different? Is that the case?

Jonathan D. Major replied: What is shown on the plot is the applied voltage.

Mirjana Dimitrievska commented: Your optoelectronic parameters have very low values, especially the efficiencies, which are <0.5% in some cases. How trustworthy are these measurements? Can we really state that we have devices in the case when efficiencies are <0.1%?

Matthew Smiles answered: I agree with the statement that with devices so low in performance it is difficult to trust an exact value for the efficiency and other values. We can certainly look at the shape of the *JV*s. Also, it can be seen clearly that there is a difference in the response under light with CdS/Sb_2Se_3/undoped GeSe compared with the other three device structures.

Mirjana Dimitrievska asked: Are your devices reproducible?

Matthew Smiles responded: Yes, within the paper (**https://doi.org/10.1039/d2fd00048b**) we have shown average device performance as well as the best device performance.

Marcus Bär enquired: Is the statement on downward band bending at the GeSe surface a result of the photoemission measurements or does it come out of solving the Poisson equation?

How significant is that finding of downward band bending considering that the photon energy (and thus depth) dependent photoemission measurements for each sample agree within the experimental uncertainty?

Matthew Smiles replied: The presence of downward band bending at the GeSe surface is known qualitatively from the photoemission data (see Fig. 2(b) in the paper, **https://doi.org/10.1039/d2fd00048b**) and the capacitance voltage (CV) results. The former enables us to determine the surface VBM to Fermi level separation, while the latter gives an estimate of the bulk VBM to Fermi level separation. An estimate of the quantitative degree of band bending is made by solving the Poisson equation using these VBM to Fermi level separation boundary conditions. We acknowledge that the two photoemission data points are not different to within the uncertainty specified. However, the bulk information from CV measurements means we are not reliant on the difference between the two photoemission data points.

Joachim Breternitz said: I am intrigued by your powder diffraction results. How did you determine the unit cell parameters here? You report a change in the unit cell volume of 1.8% between undoped and doped GeSe. Does this appear too large, given you exchange 1 in 10 000 Ge atoms for Ag through doping? Also, do you see such variations in the thin-film diffraction measurements as well?

Matthew Smiles answered: We determine the lattice parameters using the Bragg peak positions as shown in the ESI of the paper (**https://doi.org/10.1039/d2fd00048b**). We do not see any change in the thin film XRD peak positions.

David J. Fermin remarked: In Fig. 4 of the paper (**https://doi.org/10.1039/d2fd00048b**), there is remarkable contrast in the SEM images of the Ag containing materials, particularly the stack without Sb_2Se_3 (Fig. 4a). This is strong evidence of a Ag-rich secondary phase being promoted. Can you entirely discard the nucleation of metallic silver, or Ag-rich phases, during the thin-film processing? Have you performed EDX mapping on these films?

Matthew Smiles responded: We cannot rule out the presence of a Ag rich phase at the surface of the films as EDX was unfortunately not available to us at the time of measurement.

Aron Walsh commented: One point I didn't follow was the motivation for Sb_2Se_3. We know that a CdS/Sb_2Se_3 interface could be an active junction. Could you be forming an ultra-thin Sb_2Se_3 solar cell where the GeSe plays a secondary role?

Matthew Smiles replied: Yes, we cannot rule this out here. In the record efficiency paper for GeSe (see ref. 1), the improvement from 1.4% to 5.2% power conversion efficiency is too great to be attributed to the creation of an ultrathin Sb_2Se_3 device.

1 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.

Rafael Jaramillo asked: Does this material evaporate congruently?

Matthew Smiles answered: Yes, no secondary phases have been found.

Charles J. Hages opened a general discussion: I also support promoting the availability of raw data, particularly for emerging materials. It can be quite hard to trust the processed data or extracted parameters from analysis of data, as emerging materials are often very non-ideal. We have shown that even extracting basic data *IV* curves is not trivial for these emerging, often non-ideal materials. This also holds for capacitance, TRPL, *etc.* It is often important to reconsider or allow others to reanalyze the raw data, rather than having the processed parameters shared under FAIR. For example, we are currently reanalyzing TRPL data using a new method with raw data from a paper shared by Thomas Unold rather than just taking the extracted parameters from that paper. Also, it is easy to look back with a magnifying glass to the past to determine which parameters or information we should track and make available for future work. However, with emerging materials there may be new parameters or information we don't realize is important now – having FAIR raw data would help alleviate this.

Mirjana Dimitrievska commented: Open data and fair principles are very important, but we also need published standardised protocols for how to do proper measurements and analysis in order to have reliable data that can be shared.

Susanne Siebentritt remarked: Two comments on standardisation of measurements, in particular *jV* measurements:

Firstly, the critical parameter is the area and it seems very difficult to get a correct measurement of it with a standard lab microscope. EQE is generally much more trustworthy than current density.

When we send solar cells for certification, most of the time all parameters are confirmed – only our area is wrong.

Secondly, there is a reason why only 5 labs in the world can certify *jV* measurements. It is a huge effort to standardise the measurement so that it is absolute and certified. As researchers we simply don't have the time for this effort. And for important samples, we can always send them to the certified labs.

Thomas Unold commented: I think in this I agree with Susanne that the first thing would be to record what we are doing and, if there needs to be some standardization at some point, maybe we need it but the first thing will be recording all the metadata, that's the important thing. So we can very often look at what has been happening in the halide perovskites – I think it's very interesting. They had very big differences in measuring *JV*, some were measuring reverse and some forward, and with reverse measurements you get much higher efficiencies, but it wasn't recorded, so it was a big mess for at least 1–2 years, and they had to standardise this in a way. There might be cases where we have to do this, but in other cases, in the beginning to record what we are doing and making the data available and the metadata available is a very good first step.

Jake W. Bowers remarked: There is also an important difference between having a standardised measurement with good protocols of how to do it properly, and obtaining a certified measurement from a national lab. National labs are important and require traceability among themselves, however the importance in having clear documentation on the best way to obtain measurements will enable the collection of better data in the community, in general.

Jonathan J. S. Scragg commented: We've talked a lot about data, standardisation, and the quality of measurements. These are all very important. But our job is not be lab technicians, but scientists, researchers. Our role is to convert data into knowledge: to generate interpretations and explanations. Propagating and improving explanations is what will actually give us progress. If all we have is really good data, we will not get there. Is there a role for these databases in developing our explanations?

Thomas Unold replied: I think good and generalizable models can only be made with good data and sufficient statistics. In my experience we spend too much time manually searching the literature for relevant data or manually digitizing data, or we don't even find the data that are already out there. Models that we create should be tested and possibly falsified or modified.

I agree that we should not have to spend too much time on organizing, uploading data and things like that, which is why we need good tools, that will do this more or less automatically for us.

David J. Fermin remarked: In countries like the UK, Research Councils mandate that data generated with public funds 'should be made freely and openly available with as few restrictions as possible in a timely and responsible manner.'[1] Thus, I believe that there is a significant amount of data scattered in many repositories which can be easily accessible. The key question for me is, what is the most critical data we need to curate that could lead to meaningful acceleration of material discovery?

1 EPSRC Policy Framework on Research Data, https://www.ukri.og.

Thomas Unold answered: This is a good question – from my experience, it is already difficult to collect standard properties of materials, such as band gap, absorption coefficient, effective mass, mobilities and device structures from published work. You basically have to do this manually each time.

Also I am adamant about detailed reporting of processing details.

Young Won Woo communicated: As a theorist working on perovskites, it often took longer than I thought to find a reference value because the experimental assumptions differed. A database that is organized easily and user-friendly will accelerate perovskite research. However, this field changes really fast. It will be hard to trust the database if new studies are not updated continuously. I wonder if there is a proper countermeasure for this.

Thomas Unold communicated in reply: The Perovskite Database Project (https://perovskitedatabase.com) was an effort to digitize (manually) the existing literature, limited to experimental results. To keep the database updated, now tools have been developed for easy entry of new results. The FAIRmat database intends to bring together experimental and theoretical results.

Matias Valdes opened a discussion of the paper by Byungha Shin: An observation: in the paper (https://doi.org/10.1039/d1fd00056j) you mentioned that you use "electrochemical impedance spectroscopy", but I assume you use impedance to measure solar cells. So the name must be corrected. Because you are not using an electrolyte, and without an electrolyte there is no electrochemistry. The technique is just "impedance spectroscopy" and not "electrochemical impedance spectroscopy".

Byungha Shin answered: Thanks for the correction. I will fix this in the final manuscript.

Matias Valdes commented: You report a carrier lifetime, but how do you extract this from impedance measurements? These are normally dark measurements. As far as I know it is not possible to measure this parameter using standard impedance spectroscopy measurements. It is necessary to use IMPS (intensity modulated photocurrent spectroscopy). This should be clarified in the paper (**https://doi.org/10.1039/d1fd00056j**) if you have employed another technique to measure carrier life time. Thank you.

Byungha Shin replied: I agree with you. The time-constant derived from the IS measurements, which we improperly called the "carrier lifetime", is an RC time constant reflecting the change in the shunt resistance of the Sb_2Se_3 devices. We will modify the part describing the IS results.

Phillip J. Dale said: Fig. 5 of your manuscript (**https://doi.org/10.1039/d1fd00056j**) clearly shows an improvement in the open circuit voltage for the "PAT" rear passivated sample compared to the reference sample, suggesting that the rear passivation is working. However, the EQEs are nearly identical, suggesting no improvement in the current collection near the back surface. So the voltage implies less recombination at the back, but the current collection is not getting better at the back. Could you please comment on this?

Byungha Shin responded: Given the noticeable sloping in the long wavelength region (650–850 nm) of the EQE, we seem to have a carrier collection problem presumably due to either a short carrier lifetime or low carrier mobility. Despite the suppression of the back-surface recombination (hence the improved V_{oc}), J_{sc} seems to be dominated by the poor collection through the thickness of the absorber, hence, similar EQEs for both cases resulted.

Phillip J. Dale commented: As a follow up question, the "PAT + poly-TPD" sample shows a better current collection at long wavelengths, implying better collection from deeper within the sample. However, the open circuit voltage of the "PAT + poly-TPD" is nearly identical to that of the "PAT" sample. Does this imply that something else is limiting the V_{oc}, rather than back surface recombination?

Byungha Shin replied: I think the back-surface passivation was more or less taken care of by PAT alone. The role of the additional poly-TPD must be the reflection of incident light (hence the absorption of a larger number of photons near the back surface) and/or the reflection of electrons from the Sb_2Se_3/poly-TPD interface.

Nicolae Spalatu remarked: The intermixing effect is a well-known issue and it is hard to control, especially for the superstrate configuration Sb_2Se_3/CdS. You showed a quite high device efficiency with CdS and using an additional selenization processing step. Can you comment on the issue of intermixing and how to control and avoid it?

Byungha Shin responded: We have not exclusively investigated the interfacial mixing between Sb_2Se_3 and CdS. Considering the deposition temperature of 300 °C (and PAT temperature of 100 °C which is negligible compared to the growth temperature), some degree of mixing is expected. In CIGS, interdiffusion of Cd between CIGS and the CdS buffer is known to be beneficial by converting the top surface of p-type CIGS into n-type and moving the p–n junction away from the metallurgical CIGS/CdS interface. A similar mechanism may operate in the case of Sb_2Se_3 too.

Nicolae Spalatu commented: A 300 °C deposition/annealing temperature is quite high. A current of 30 mA is very impressive for Sb_2Se_3 in combination with a CdS buffer layer. Could you comment on such a large value of the current density for the device with CdS, having a band gap of 2.5 eV and parasitic absorption at 350–400 nm wavelength?

Byungha Shin answered: We found that the key to high J_{sc} in Sb_2Se_3 solar cells was the proper crystallographic alignment of the absorber along the [*hk*1] direction. The parasitic absorption by the CdS is reflected in low EQEs (~50%) between 400 and 500 nm, which we believe accounts for the loss of J_{sc} of 2 mA cm^{-2} maximum.

Marcus Bär asked: What is the ion energy you use for your depth profiling when sputtering through the sample? Are you not afraid of sputter-induced artefacts?

Byungha Shin replied: We used an Ar ion beam at 2 keV. Given that almost identical spectra were obtained from the "After PAT" sample during the depth profiling (Fig. 2b and d in our paper, **https://doi.org/10.1039/d1fd00056j**), we believe any sputter-induced artifacts were minimal.

Jonathan D. Major remarked: Following on from Phillip J. Dale's question – there seems to be a degree of overlap between the poly-TPD approach and the PAT effect. There is a similar increase for addition of the TPD to with the PAT. Did you introduce poly-TPD for a device that was not PAT to separate the effects?

Byungha Shin responded: This is a good suggestion. Unfortunately we have not examined the case where only poly-TPD was applied without PAT. However, we tried other HTL materials (PTAA, spiro, PEDOT:PSS and TFB) without PAT. Compared to the reference (without any HTL and without PAT) they all improved J_{sc} and all except TFB improved V_{oc}. Therefore, we could conclude that there is a substantial overlap in the back-surface passivation by the PAT and an HTL.

Thomas P. Weiss commented: In the paper (**https://doi.org/10.1039/d1fd00056j**) the lifetime is calculated from $R_{REC} \times$ CPE. However, this quantity is not the carrier lifetime, but the RC time constant. Thus, the time-constant rather reflects the improved shunt resistance.

Byungha Shin answered: I agree with your interpretation. We would need to make another measurement such as time-resolved PL to access carrier lifetime.

Xinwei Wang remarked: In your paper (**https://doi.org/10.1039/d1fd00056j**), you mentioned the formation of antimony oxides under Sb-rich conditions.

Firstly, are they inside the bulk or at the interface? Secondly, some papers also reported that the formation of a thin Sb_2O_3 layer under Sb-rich conditions benefits the efficiency because it may passivate the interfacial defects. But you also mentioned in your paper there will be more detrimental bulk defects under Se-rich conditions. Does this mean the harmful effects of bulk defects and interfacial defects cannot be alleviated at the same time?

Byungha Shin replied: From XPS depth-profiling, we confirmed that antimony oxide resides on the surface. Even for an Sb_2Se_3 film treated with post-deposition Se annealing (*i.e.*, detrimental V_{Se} residing in the bulk taken care of), there is a thin layer of Sb_2O_3 even though it is thinner than the oxide layer on Sb_2Se_3 with no post-deposition Se treatment. Therefore both surface and bulk defects can be passivated in the case of post-deposition Se treatment.

Theodore Hobson asked: Were you able to measure the valence band position region with photoemission?

Byungha Shin answered: In theory we should have been able to locate the valence band position with the XPS spectrum by examining the low binding energy part of the spectrum corresponding to photoelectrons from valence electrons. However, the X-ray cross-section at the low BE part is small and therefore the signal is noisy. We are better off using UPS for this. We haven't measured UPS yet but plan to do so in the near future.

Theodore Hobson commented: In our experience we have found it quite difficult to fit core level positions with sufficient precision to track small changes in the positions of the valence band, for instance due to band bending, and so found it necessary to fit the valence band itself.

Byungha Shin replied: I would recommend UPS measurements to find the position of the valence band independently.

David J. Fermin opened a discussion of the paper by Nicolae Spalatu: It is rather surprising to see changes in lattice parameters as a result of the removal of residual organic impurities in titania. On the other hand, vacuum annealing will promote oxygen vacancies which can affect the lattice constant, perhaps under rather extreme conditions. Can you elaborate on why you link structural changes to organic residues rather than structural defects?

Nicolae Spalatu responded: The changes in the lattice parameters of TiO_2 can occur as a result of both the removal of residual impurities, and the generation of oxygen vacancies under vacuum annealing conditions. We linked the structural changes to organic residues as the mobility of these residuals is very intensive at both low–moderate and at higher vacuum and air annealing temperatures.

On the other hand, within the same process, the carbon impurity incorporates into the lattice and probably also accumulates at the grain boundaries of TiO_2, as suggested by the results of XPS analysis. Incorporation of carbon atoms into the lattice of anatase TiO_2 can occur through a substitutional mechanism at the oxygen sites and/or by taking an interstitial site.

Rokas Kondrotas commented: Impurities can play an important role in heterojunction formation. You found C in TiO_2 films, but it is not clear if it was surface contamination or bulk. So the question is have you an idea of how C impurities change the TiO_2 electronic structure when they are on the surface and when they are in the bulk?

Nicolae Spalatu replied: Incorporation of carbon atoms into the lattice of anatase TiO_2 can occur through a substitutional mechanism at the oxygen sites and/or by taking an interstitial site. Thus, the carbon impurity may introduce localized states through which the electrons are trapped and thereby decrease the overall electron concentration.

Marcus Bär asked: Do you have any insights on whether the C you observe in your sample also forms Ti–C bonds, *i.e.*, have you recorded the detailed spectrum of Ti 2p? Do you see a low binding energy shoulder that could be attributed to Ti–C bonds?

Nicolae Spalatu answered: Unfortunately, we do not have deep insights into this. However, we do agree that such a binding energy shoulder could be attributed to Ti–C bonds and should be investigated more thoroughly.

Jake W. Bowers said: In the V_{oc} and J_{sc} *vs.* temperature data, there is a large drop in the V_{oc} from 300 to 350 °C in air; however you don't present the corresponding vacuum annealed data below this temperature range. Why is that?

Nicolae Spalatu responded: Indeed we did not present the V_{oc} and J_{sc} *vs.* temperature data for vacuum annealing below 300 °C. This is because below this temperature the TiO_2 films were amorphous and it is well known that these layers will not work in a solar cell device with this configuration.

Joachim Breternitz asked: Are you aware which phase of TiO_2 you form? Rutile is the most stable phase in the bulk, but anatase becomes the most stable phase for smaller crystallite sizes. Would this potentially have a larger effect than residual carbon?

Nicolae Spalatu replied: According to XRD and XPS analysis, the TiO_2 films annealed in a vacuum and in the air at 300–500 °C exhibit the anatase phase.

Joachim Breternitz commented: In addition to the previous question: TiO_2 tends to lose oxygen at higher temperatures, compensated through the reduction of Ti^{4+} to Ti^{3+}, which then becomes blue. Have you observed any such colour change?

Nicolae Spalatu answered: We did not observe any changes in the color of the TiO_2 films annealed in a vacuum at 200–450 °C.

Byungha Shin remarked: We found that the photocurrent from Sb_2Se_3 solar cells is quite sensitive to the crystallographic orientation of the Sb_2Se_3 absorber. As a way to quantify the crystallographic orientation we use the ratio of peak intensity of (221) to (120). When this value is above 10 we get a good photocurrent. What is a typical value of this ratio, (221)/(120) in your case?

Nicolae Spalatu responded: It is widely accepted that the crystallographic orientation of the Sb_2Se_3 significantly impacts the PV parameters of the solar cells. However, in our case, we did not detect (120) orientation in the diffractogram of Sb_2Se_3 deposited by close space sublimation.

Nicolae Spalatu asked: What could be a suitable characterization method to study more thoroughly the solar cell device interface and recombination at the interface (to quantify the recombination rates at the interfaces)?

Devendra Tiwari replied: If this is a general question regarding PV device characterisation, then this is quite a loaded one, deserving volumes of handbooks indeed. To begin with, what sort of materials and device structure are we talking about – small-molecule or polymeric organic bulk heterostructure, or inorganic junctions? For the context of this meeting, I am assuming and constraining to the latter. Even then, defining the interface depends on a few different pieces of information such as the actual set of materials – composition and morphology, device architecture, junction type and ideality of the interfacial chemistry (or its resemblance to respective bulk characters) which would restrict the set of techniques and models to analyse the data that could be implemented. More importantly, the most non-trivial part is tunability of the probe and the setup to distinguish and separate the transport dominant at interface from that in the bulk.

Typically, in (opto)electronic measurements, one could either use light or potential bias, guided by the chemical and structural characterisation, to probe across the thickness of the device and/or the electrical junctions. Lastly, the most accessible techniques and most commonly employed degree of analysis tell us about the energetic positions, abundance of recombination sites and, in occasional cases, if we have enough information, defect cross-section as well. Since the overall power conversion efficiency is a steady-state feature, the knowledge and direct measurement of the recombination kinetics become inconsequential in most cases or are inferable from the drift–diffusion equations, as typically most device modelling implementations do in the backend. The most direct measurement of transport parameters related to interfacial recombination is, perhaps, through a dynamic measurement of quasi-Fermi levels and carrier recombination velocities – which is challenging to do, to say the least, and perhaps would be more doable for well-defined surfaces (and not complex interfaces) as has been demonstrated in a few limited cases.

However, I will mention a few techniques, familiar to me, which come close to this though none would be straightforward to analyse and generalise to characterisation of PV devices.

(i) Absolute photoluminescence (PL) measurement or PL quantum yield if the excitation is tuned to be interactable only within the interfacial region and most of the depletion occurs on one side of the junction (absorber). Then, the yield and peak width can be used to model the recombination kinetics. (ii) From the attempt-to-escape frequency term (or its analogues) appearing in models used for capacitance-based (or other) techniques convoluted in the pre-exponential factor.

Techniques such as temperature-dependent admittance or deep-level transient spectroscopy are worth mentioning in this case. The latter being informationally more comprehensive but more difficult to analyse. (iii) Time-of-flight methods, transient photovoltage, charge-extraction and allied methods including IMPS and IMVS, the analysis of which requires complementation from other semiconductor transport measurements and/or specific sample preparation. Of course, the caveats are (a) as the number of parameters to be deduced in the model increases, one would have to include more physical variants such as temperature and/or intensity *etc.*, (b) precise and independent knowledge of other fundamental semiconductor parameters, including density of state near band-edges, (c) applicability of the particular technique and setup to probe the required lifetimes, and (d) most restrictively, a careful sample preparation well suited for clean measurement and analysis. In particular, the last often forbids conducting and analysing such measurements for low performing, albeit most interesting, devices of emerging materials where little is known to enable such detailed analysis. Further, as an aside it's important to note here that the composition, bonding and electronic structures at surfaces especially for (non-textbook) compound semiconductors can vary significantly from the bulk and therefore most optoelectronic, chemical and semiconductor transport parameters will be significantly different as well. Added on to that is the complexity endowed by the polycrystalline nature of the materials, as is preferable for use in large scale deployable applications. This will have knock-on effects on a universe of information taken as the same as the bulk, most influentially charge–phonon coupling.Finally, as a material scientist and perhaps as alluded to by Dr Spalatu, knowing the thermodynamics and kinetics of carrier recombination is not of much help without the related chemical information, which then can be used to rationally modify materials and devices for better performance. The simultaneous or correlatable determination of chemical information and carrier-transport and validity of such methodology would be a whole different story.

So, in the end, the dynamic and multi-faceted distinguishable characterisation of the interface and bulk carrier transport for optoelectronic devices is the next frontier indeed. For now, the applicability and relevance of a measurement technique for ascertaining the interfacial recombination will, therefore, be on a case-by-case basis and more so than as prevalently assumed for the bulk.

Mingqing Wang commented: TiO_2 has been widely used as an electron transport layer in dye-sensitised solar cells (DSSCs). Normally the TiO_2 film is thermally annealed above 500 °C to remove the carbon residue from the precursor and improve the crystallization of the deposited (by spray pyrolysis or spin coating) thin films. $TiCl_4$ treatment is widely used to passivate the surface defects of the TiO_2 electron transport layer. I wonder why you selected the maximum temperature of 450 °C for the thermal treatment of the TiO_2 thin film in your work (**https://doi.org/10.1039/d2fd00064d**)? Do you plan to explore the application of your device structure on a flexible substrate later?

Nicolae Spalatu answered: We have tried both 450 and 500 °C annealing temperatures and no differences have been observed. That's why we've chosen a lower annealing temperature – imperative for an energy-saving PV technology.

Phillip J. Dale remarked: There are other methods than ultrasonic spray pyrolysis to deposit TiO_2. Would it not make more sense to use a sputtered TiO_2 sample to rule out the influence of carbon? That would allow you to de-couple the heating of your sample from the carbon content.

Nicolae Spalatu responded: Sputtered TiO_2 could be an option to de-couple the effect of organic residuals. Our preliminary studies (not yet published) show that Sb_2Se_3 cells processed with sputtered TiO_2 (as a heterojunction buffer layer) have significantly lower efficiency compared to the device obtained with sprayed TiO_2 films. This might be related to the highly resistive behaviour of perfectly stoichiometric sputtered TiO_2.

Phillip J. Dale asked: Do you need the carbon impurities in the TiO_2 for it to function as you would like?

Nicolae Spalatu replied: According to our solar cell results, the higher the concentration of the carbon impurity the lower the efficiency of the Sb_2Se_3/TiO_2 device. This leads to the conclusion that the carbon impurity in TiO_2 has a negative impact on the formation of a heterointerface in the related device.

Byungha Shin said: You mentioned the TiO_2 in your Sb_2Se_3 devices is defective. If you mean electrically leaky by defective, I would suggest that you try e-beam deposited TiO_2, which tends to be electrically conducting.

Nicolae Spalatu answered: Thank you for your suggestion. It would be worth trying such an experiment.

Rokas Kondrotas addressed Byungha Shin: I have a question regarding $CdCl_2$ treatment on CdS. I was wondering what kind of PCE you achieved without $CdCl_2$ treatment. Which solar parameters did it affect most? Have you tried other treatments?

Byungha Shin replied: We were getting around 5.5–6% PCE without $CdCl_2$ treatments. The parameter that was improved the most after the treatment was J_{sc} by as much as 3 mA cm^{-2}. V_{oc} and FF remained similar.

Jonathan J. S. Scragg said: You talked about Se vacancies in antimony selenide. It would be instructive to compare the Se vacancy formation energy in antimony selenide with that in the more well-known CZTSe kesterite. Are they similar?

Byungha Shin responded: The formation energy of Se vacancies depends on the Fermi level and composition (Se rich *vs.* Se poor). According to DFT calculations, in Sb_2Se_3, the formation energy of V_{Se} ranges from 0.6 to 1.4 eV under Se-rich conditions and from 0.2 to 1.0 eV under Se poor conditions. In CZTSe, it is from 2.3 to 3.0 eV. See Fig. 1 and 2 which include the formation energies of various point defects in Sb_2Se_3 and CZTSe from the literature.

1 X. Liu, X. Xiao, Y. Yang, D.-J. Xue, D.-B. Li, C. Chen, S. Lu, L. Gao, Y. He, M. C. Beard, G. Wang, S. Chen and J. Tang, *Prog. Photovolt.: Res. Appl.*, 2017, **25**, 861–870.

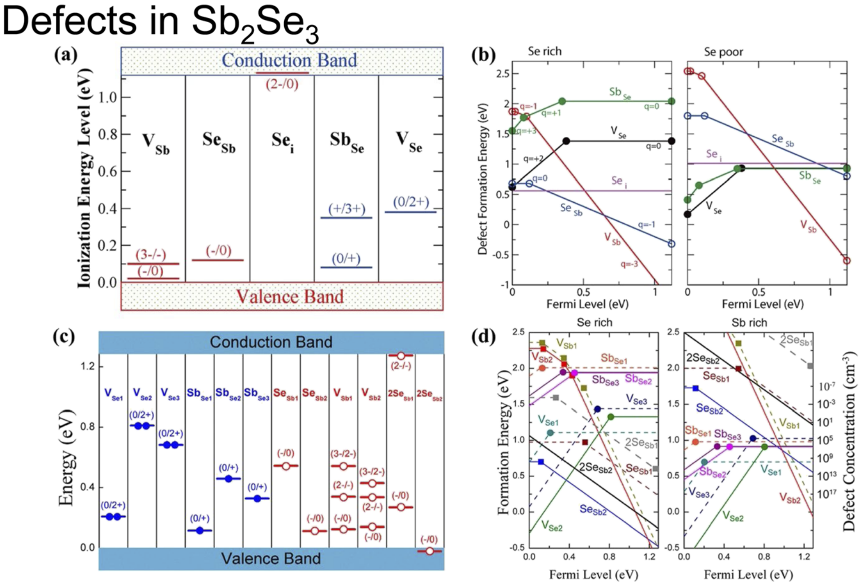

Fig. 1 (a) and (c) Ionization energies of various point defects in Sb_2Se_3. (b) and (d) Formation energies of various point defects in Sb_2Se_3. (a) and (b) are reproduced from ref. 1. (c) and (d) are reproduced from ref. 2.

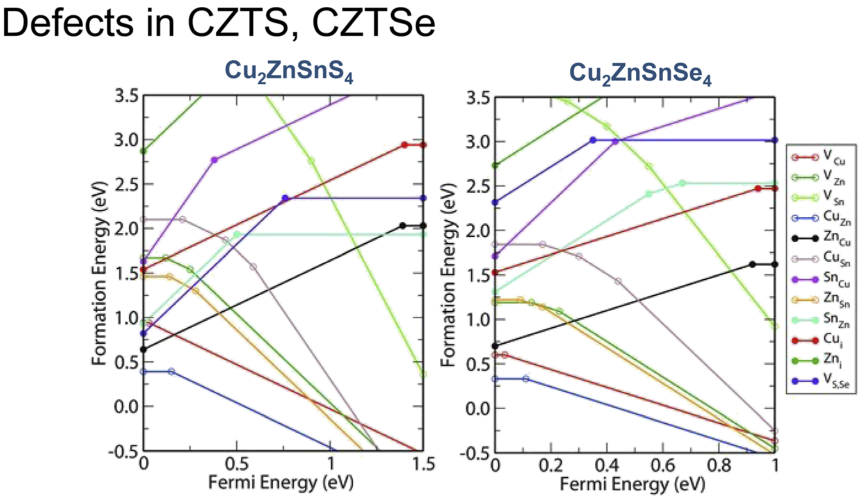

Fig. 2 Formation of various point defects in CZTS and CZTSe. Reproduced from ref. 3.

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2 M. Huang, P. Xu, D. Han, J. Tang and S. Chen, *ACS Appl. Mater. Interfaces*, 2019, **11**, 15564–15572.

3 S. Chen, A. Walsh, X.-G. Gong and S.-H. Wei, *Adv. Mater.*, 2013, **25**, 1522–1539.

Jonathan J. S. Scragg remarked: Just like for kesterites, you seem to get better performance for higher Se pressure – for example, as you know, co-evaporated kesterites never achieved the same performance as those made using two-stage processing with a high chalcogen pressure. One possible cause is that Se vacancies are "killer defects" – this has been proposed for kesterite based on calculations. Although we improve the situation with a high Se pressure, it is not certain that it is fully resolved, and that all Se vacancies are eliminated. Do you think there could be parallels between the case of Sb_2Se_3 and that of kesterite?

Byungha Shin answered: Based on theoretical work (for example, ref. 1), the energy level of Se vacancies is close to the mid-gap and therefore they are expected to be "killer defects" as in kesterite, which is also experimentally supported by the improved performance (especially V_{oc}) with Se flux both during and after the deposition. We believe the density of Se vacancies can be reduced to a negligible level based on the following PL measurements and the interpretation (Fig. 3).

To estimate the concentration of point defects in Sb_2Se_3, we conducted low-temperature PL at $T = 10$ K. We examined two samples, Sb_2Se_3 films grown without Se and with 40 mg Se. In both cases, there is a peak at 1.31 eV, which is labelled as P2. The room-temperature bandgap of Sb_2Se_3, derived from the EQE, is ~1.16 eV. Considering the temperature dependence of the bandgap of Sb_2Se_3, we attribute the PL peak at 1.31 eV at 10 K to the band-to-band recombination. Additionally, there is another peak at ~1.22 eV (labelled P1), which must originate from recombination through traps, either 0.09 eV below the conduction band edge or 0.09 eV above the valence band edge. Based on theoretical studies in the literature, the traps giving rise to P1 are shallow acceptor-like defects, Sb vacancies (V_{Sb}). The relative ratio of P1/P2 allows us to estimate the relative population of V_{Sb} between the two samples (no Se *vs.* 40 mg Se). Another piece of information learned from the previous theoretical studies is the difference in the formation energy of various point defects, from which we could also determine the ratio of their equilibrium concentrations. In Se-poor conditions (relevant for the no Se

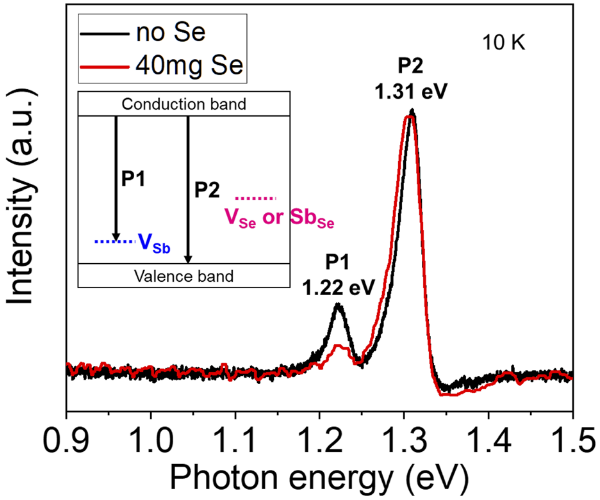

Fig. 3 Comparison of low temperature (10 K) PL spectra of Sb_2Se_3 prepared with and without additional Se flux.

sample), the formation energy of V_{Sb} in weakly p-type Sb_2Se_3, which is the case for our Sb_2Se_3 films as confirmed by UPS, was reported to be similar to that of V_{Se}; therefore, their equilibrium concentrations must be very similar, too. On the other hand, in Se-rich conditions (relevant for the 40 mg Se sample), the formation energy of V_{Se} is substantially larger than that of V_{Sb} by 1.2 eV. With this large difference in the formation energies, the estimated ratio of the equilibrium concentration of V_{Se} to that of V_{Sb} is almost 1×10^{-13}; therefore, the concentration of V_{Se} in an Sb_2Se_3 film prepared under Se-rich conditions as for the 40 mg Se sample is negligible compared to V_{Sb}. From the PL measurements of the two samples (no Se *vs.* 40 mg Se), the ratio of P1/P2 is smaller in the case of 40 mg Se suggesting that the concentration of V_{Sb} is also smaller. Now considering the estimated ratio of the concentration of V_{Se} to that of V_{Sb} is 1×10^{-13} in the 40 mg Se sample, while the ratio must be close to 1 in the no Se sample, it is fair to conclude that the concentration of V_{Se} in the 40 mg Se sample is much smaller than that in the no Se sample by more than 10 orders of magnitude – to an almost negligible level.

1 X. Liu, X. Xiao, Y. Yang, D.-J. Xue, D.-B. Li, C. Chen, S. Lu, L. Gao, Y. He, M. C. Beard, G. Wang, S. Chen and J. Tang, *Prog. Photovolt.: Res. Appl.*, 2017, **25**, 861–870.

Nicolae Spalatu commented: Vacancy type defects such as Se-vacancies, and vacancies of antimony play a major role in the properties of Sb_2Se_3. In your opinion, which of these defects has a more detrimental impact on the device performance?

Byungha Shin responded: According to theoretical work reported in the literature (see ref. 1–3), V_{Sb} is a shallow defect contributing to the p-type conductivity of Sb_2Se_3 while the energy level of V_{Se} is close to the mid-gap. Therefore, V_{Se} must be more detrimental for the device performance.

1 X. Liu, X. Xiao, Y. Yang, D.-J. Xue, D.-B. Li, C. Chen, S. Lu, L. Gao, Y. He, M. C. Beard, G. Wang, S. Chen and J. Tang, *Prog. Photovolt.: Res. Appl.*, 2017, **25**, 861–870.
2 M. Huang, P. Xu, D. Han, J. Tang and S. Chen, *ACS Appl. Mater. Interfaces*, 2019, **11**, 15564–15572.
3 S. Chen, A. Walsh, X.-G. Gong and S.-H. Wei, *Adv. Mater.*, 2013, **25**, 1522–1539.

Sreekanth Mandati said: In Sb_2S_3 solar cells, the open circuit voltage deficiencies are attributed to self trapping of carriers due to lattice deformation as reported by Yang *et al.*[1] as opposed to the intrinsic defects. This sets the maximum attainable V_{oc} to be limited to 0.8 V. Can someone comment and provide some insights on this? Thanks.

1 Z. Yang, X. Wang, Y. Chen, Z. Zheng, Z. Chen, W. Xu, W. Liu, Y. Yang, J. Zhao, T. Chen and H. Zhu, *Nat. Commun.*, 2019, **10**, 4540.

Byungha Shin replied: At least for Sb_2Se_3, we saw indirect but clear evidence that point defects such as V_{Se} strongly influence V_{oc}. It is possible that both self-trapping and intrinsic defects matter.

Prakriti Kayastha communicated: There have been several discussions during the conference about how oxygen bonding is fundamentally very different to S or Se bonding. In Fig. 3 of your work (**https://doi.org/10.1039/d1fd00056j**), both

Sb_2O_3 and Sb_2Se_3 seem to have very similar vibrational behaviour, except for the green 'A_g' band. Could you comment?

Byungha Shin communicated in reply: You are right about the vibrational spectra of Sb–O and Sb–Se bonding. In Fig. 3 of the paper (**https://doi.org/10.1039/d1fd00056j**), both samples are Sb_2Se_3 (with a thin layer of Sb_2O_3 on top). The green line at $\sim$255 cm^{-1} represents the A_g band of the oxide, which is present in both samples because there is a surface oxide layer on both samples, although the intensity is weaker for the PAT sample, consistent with XPS results. The peaks at $\sim$115 and $\sim$190 cm^{-1} represent the A_g bands of the selenide, which are different from the A_g band of the oxide.

Conflicts of interest

There are no conflicts to declare.