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Indium-free CIGS analogues: general discussion

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Rafael Jaramillo opened discussion of the introductory lecture by David Mitzi: What is your most trusted approach to accurately measure the absorption coefficient on a new thin film material?

David Mitzi replied: The point about significant challenges in making and evaluating reliable absorption measurements for emerging thin-film absorber materials is a good one. In general, absorption measurements using UV-Vis spectroscopy can be influenced by film roughness and scatter, as well as a number of other prospective complications. In terms of using these measurements to extract a bandgap value, we often make use of the long wavelength cut-off in the quantum efficiency (QE) curve, since this allows us to directly extract a bandgap value on a device-relevant film. Although there are various methods for extracting the bandgap from this curve, we generally use a derivative method (*i.e.*, taking the derivative of the QE with respect to wavelength or energy and selecting the peak in this function at the long wavelength cutoff). This approach of using the inflection point of the QE curve in the region of the absorption threshold is also a suggested method of bandgap extraction put forward in a recent *Adv. Energy Mater.* article that benchmarks emerging photovoltaic technologies as a function of bandgap value.[1]

[1] O. Almora *et al.*, *Adv. Energy Mater.*, 2021, **11**, 2002774, DOI: **10.1002/aenm.202002774**.

Charlotte Platzer Björkman asked: The $Zn_{1-x}Cd_xS$ buffer layer had quite a minor increase in band gap energy and was not optimal in terms of conduction band alignment. Was that due to a limit in zinc addition in the deposition process?

David Mitzi answered: The zinc content is not limited by the SILAR process, as previously shown by the UNSW (Xiaojing Hao) group (*e.g.*, see ref. 1 and 2). We tried higher zinc content in our buffers for the CBTSSe devices. However, these buffers did not lead to higher PV performance (or even V_{oc}). One hypothesis is that, for higher zinc content, the doping level in the buffer may drop, which may counteract the benefit of the higher conduction band (lower electron affinity). However, these are very recent results and we will need to further examine this issue to see what factors are controlling performance in the devices employing higher zinc content buffers.

1 K. Sun, C. Yan, F. Liu, J. Huang, F. Zhou, J. A. Stride, M. Green and X. Hao, *Adv. Energy Mater.*, 2016, **6**, 1600046, DOI: **10.1002/aenm.201600046**.

2 K. Sun, C. Yan, J. Huang, F. Liu, J. Li, H. Sun, Y. Zhang, X. Cui, A. Wang, Z. Fang, J. Cong, Y. Lai, M. A. Green and X. Hao, *J. Mater. Chem. A*, 2019, **7**, 27289–27296, DOI: **10.1039/c9ta09576d**.

Susanne Siebentritt said: I don't think high dispersion bands and low effective mass are as important as you state. With high masses we get a higher density of states and a higher absorption coefficient and can live with thinner absorbers – which need less good transport, see ref. 1.

1 T. Kirchartz and U. Rau, *Sustainable Energy Fuels*, 2018, **2**, 1550–1560, DOI: **10.1039/c7se00622e**.

David Mitzi responded: This is a great point. The parameters that I mentioned for targeting high-performance absorbers are often coupled. So increasing the band dispersion to improve carrier mobility can reduce joint density of states at the band edge and therefore absorption coefficient. In this sense, optimizing absorber performance can often involve balancing several competing effects (which may include, for example, needing to use a thinner absorber layer to allow for better charge extraction). Nevertheless, given the coupling of minority carrier diffusion length with carrier mobility values, I would still maintain that targeting a reasonable band dispersion (and associated minority carrier mobility and diffusion length) is still an important target for new absorbers. Notably, small band dispersion can also lead to carrier localization and polaron formation, which is detrimental for PV performance.[1]

1 A. Walsh and A. Zunger, *Nat. Mater.*, 2017, **16**, 964–967, DOI: **10.1038/nmat4973**.

Cara Hawkins enquired: You emphasised in the introduction to your talk about the importance of targeting materials based on earth abundant and non-toxic elements, for example moving away from Cd in solar absorbing materials. However in the devices you have developed you include a CdS buffer layer. Do you have any suggestions for how moving forward we can remove Cd from this layer, or how we can base layers included in device architectures on more abundant and less toxic elements?

David Mitzi answered: Excellent question. Optimizing device structures is much more challenging than simply focusing on the absorber, given a large number of interfaces that need to be considered in the device. The process of selecting a suitable buffer material, for example, involves not just considering band offsets and doping of the buffer relative to the absorber, but one also needs to be concerned about the chemical interaction (potential ion migration and reactivity) at the interface with the absorber. In this regard, trying to identify a buffer material that both satisfies the needs of good electronic/chemical match with the absorber, as well as being earth abundant and non-toxic, poses a significant (though also important) challenge for future research to address. The ZCS ($Zn_{1-x}Cd_xS$) in our research was meant to be a starting point for addressing the conduction band cliff problem in CBTSSe. This approach was selected because ZCS provides a convenient and demonstrated means to tailor the conduction band edge by varying the Zn : Cd ratio (*i.e.*, as shown in ref. 1). By using this readily available system, we wanted to prove the importance of the conduction band offset in controlling the V_{oc} deficit. Future work will be targeted towards trying to refine this approach and to move to more environmentally friendly materials. Buffer systems of possible interest might include, for example, zinc oxysulfide or doped zinc magnesium oxide, which might offer similar opportunity for optimizing the electron affinity of the buffer, but without the use of highly toxic cadmium.

1 K. Sun, C. Yan, F. Liu, J. Huang, F. Zhou, J. A. Stride, M. Green and X. Hao, *Adv. Energy Mater.*, 2016, **6**, 1600046, DOI: **10.1002/aenm.201600046**.

Mohit Sood queried: When you increase Zn concentration in CdZnS, with the increase in conduction band you see lower doping. As a consequence the device performance does not improve. Maybe because the inversion at the junction is not that good. Can we mitigate this if we use a thinner buffer layer, or rather than using a ZnMgO i-layer, a doped ZnMgO layer instead – will that help?

David Mitzi replied: If it is possible to make a quality buffer thinner, this may help in terms of reducing parasitic absorption in this layer and, additionally, a thinner layer may be less problematic in the context of a low doping density. However, there are challenges associated with thinning the buffer substantially – *e.g.*, avoidance of pinholes and shunting. So, in this sense, there are limits as to how thin a buffer can be made (we explored this in the context of CZTS devices in ref. 1). Doping of higher bandgap buffer prospects like ZnMgO could also be attractive, assuming a suitable doping scheme can be developed.

1 M. T. Winkler, W. Wang, O. Gunawan, H. J. Hovel, T. K. Todorov and D. B. Mitzi, *Energy Environ. Sci.*, 2014, 7, 1029–1036, DOI: **10.1039/c3ee42541j**.

Phillip J. Dale asked: Some of your new target compounds contain elements which contain multiple oxidation states which are energetically easily accessible. What I remember from working on the tin containing kesterite compounds is the +2, +4 oxidation states and how one of these provided detrimental defect levels in the band gap. One of the compounds that your group is targeting is Cu_2PbGeS_4; I believe Pb also easily forms either +2 and +4 oxidation states. Do you think the issue of multiple oxidation states will also be relevant here?

David Mitzi answered: Indeed, this issue of metal oxidation state stability was one driving force behind our looking at $Cu_2BaGeSe_4$ (CBGSe) in relation to Cu_2BaSnS_4 (CBTS), in that we felt that CBGSe might be less susceptible to Ge^{2+}-related defects, since Ge^{2+} is presumably more difficult to access than Sn^{2+} (*i.e.*, in relationship to corresponding tetravalent states). Further, there was the consideration that Ge^{4+} offers a more differentiated ionic size relative to Cu^+, compared with Sn^{4+}, and the hope was that this would provide less driving force for anti-site disorder. Sadly, despite these expectations, the deep defect properties of CBGSe seem to be worse relative to CBTS, according to our low temperature photoluminescence measurements (*e.g.*, see ref. 1). So clearly more work needs to be done to understand the nature of defects in CBGSe. Regarding the Pb-based system, we have not specifically addressed the question of Pb^{2+} *vs.* Pb^{4+} (*e.g.*, using DFT analysis). Nevertheless, I believe that the 2+ state is relatively stable for Pb among metal chalcogenides. So hopefully, this would not be a significant issue for the Cu_2PbGeS_4 system. However, more detailed computational and experimental analysis would be needed to definitively address this point. I think that, overall, our experiences with CBGSe highlight a general need for better experimental approaches for understanding the chemical origins of defect states in complex chalcogenide semiconductors. Such approaches would make it easier to close the loop on corresponding computation-based analyses.

1 Y. Kim, H. Hempel, S. Levcenco, J. Euvrard, E. Bergmann, O. Gunawan, T. Unold, I. G. Hill and D. B. Mitzi, *J. Mater. Chem. A*, 2021, **9**, 23619–23630, DOI: **10.1039/d1ta05666b**.

Phillip J. Dale queried: I very much like your question about compound simplicity *versus* complexity (few *versus* many elements). Given that the compounds you are investigating comprise four elements, which need to be deposited uniformly over meters squared, I agree that this is academically fun and interesting, but is it industrially relevant?

David Mitzi responded: I believe that experiences with CIGS point to the fact that, in principle, the simpler the system the better in terms of providing for low cost and high yield fabrication approaches. So if an elemental or binary system can provide all the properties that are desired for a photovoltaic absorber, this would probably be a better path to pursue. However, there are also advantages in terms of tunability that can be provided by having more chemical complexity (*i.e.*, pursuing multinary systems). For example, having multiple chemical sites within a semiconductor can allow for independently shifting the valence and conduction band edges, as well as provide a pathway for introducing band gap grading within the device. However, this tunability needs to be balanced against the increased number of pathways for defect formation (*i.e.* proliferation of possibilities for anti-sites, vacancies and interstitials) when more elements are involved in the semiconductor. This is one reason why we want to understand possible design principles for such multinary systems that can be used to control disorder (*e.g.*, as mentioned in ref. 1).

1 D. Shin, B. Saparov and D. B. Mitzi, *Adv. Energy Mater.*, 2017, **7**, 1602366, DOI: **10.1002/aenm.201602366**.

Rachel Woods-Robinson asked: As has been discussed, many known thin film absorber materials are solid solutions off-stoichiometry rather than on-stoichiometric compounds (*e.g.*, $CdSe_xTe_{1-x}$, SbS_xSe_{1-x}), which enables tunability of properties. However, most of our computational screenings first look for *compounds*, identify a compound of interest that emerges from the screening, and then move off-stoichiometry in the lab to grow alloys associated with an endpoint compound. This can induce properties shifted from those that have been predicted, and this approach may also miss materials in which the endpoint compound does not emerge from a screening but a solid solution does. Should we perhaps be inverting our searches and first targeting solid solutions with good properties? Or, for a given compound, should we be searching for a range of tolerance of properties rather than just on-stoichiometric properties?

David Mitzi answered: That is an interesting question. From the point of view of a materials designer (involving perhaps a confluence of theory and experiment) it is easier to start from a simpler system and move to more complex ones. I believe that this fact really underlies the general approach of starting from the endpoints and then later considering more complex alloyed or off-stoichiometric versions. So in my talk (**https://doi.org/10.1039/d2fd00132b**), one example involved starting with the endpoint compounds Cu_2BaSnS_4 and $Cu_2BaGeSe_4$ (even though they don't have the most appropriate bandgaps for single-junction PV), and then moving to the more complex systems – *e.g.*, $Cu_2BaSnS_{4-x}Se_x$ or $Cu_2BaGe_{1-x}Sn_xSe_4$. The simpler compounds provide a good baseline to understand how the properties evolve under alloying. That being said, I certainly understand the point that one often needs to have solid-solution or off-stoichiometric materials in order to get the best photovoltaic properties. CIGS provides a good example for this, whereby mixtures of Ga and In (or S and Se) and shifting to Cu-poor stoichiometries is important for getting the best properties. So I agree that there may be limitations in the approach of focusing on better-ordered endpoint compounds as the starting point of our studies (*e.g.*, maybe certain systems behave better as alloys than others and so the endpoints may not be representative of the ultimate potential of the alloys). On the other hand, I don't have an immediate good suggestion as to how to implement an efficient materials search that starts with an intentional target of solid solutions. Maybe this might be a reasonable target for machine learning approaches to try to tackle?

Jens Wenzel Andreasen opened discussion of the paper by Charlotte Platzer Björkman: You mentioned that it appears to be easier to obtain a good morphology in the thin absorber layers. Do you know what a good morphology is, and how do you determine if you have it?

Charlotte Platzer Björkman responded: Most likely large grains extending from top to bottom is good as well as absence of voids and secondary phases.

Joachim Breternitz asked: I am wondering what the chemical role of NaF is? You show increased performance when bringing NaF on top of the kesterite layer as opposed to depositing it between passivation layer and kesterite layer. Does NaF therefore interact with the kesterite, which in turn interacts with the passivation layer?

David Mitzi added: With regards to the better kesterite device properties when NaF is placed on top of the thin absorber during processing (rather than at the back of the absorber, on top of the passivation layer), might the improvements be related to the more efficient access of the NaF layer to the chalcogen vapor during the sulfurization part of the processing?

Also, as mentioned in some earlier papers (*e.g.*, see ref. 1), NaF decomposition may be facilitated by formation of SF_6 (SeF_6) during the sulfurization (selenization) process, whereas this process may be less efficient when the NaF is placed at the back of the absorber film. More facile decomposition of NaF may in turn provide a more rapid boost in Na content within the film during processing and therefore enable better absorber characteristics. Perhaps this factor might contribute to improved performance when the NaF is placed at the top of the absorber during processing?

1 A. Laemmle *et al.*, *J. Appl. Phys.*, 2014, **115**, 154501, DOI: 10.1063/1.4871457.

Charlotte Platzer Björkman replied: Thank you for pointing this out. The question then is if we could detect differences in the F concentration through the layers, and this would be interesting to do. Regarding absorber qualities, we do not have the comparison between devices made with NaF on top of the CZTS precursor and the ALD Al_2O_3 since the latter samples peeled. In the case of HfO, we do have that comparison. For several samples, partial peeling and pinholing was worse with NaF on the HfO, but in one case device performance was similar to those with NaF on top of the precursor, or even better. The NaF treatment both influences the charge transport through the passivation layer and most likely also electronic properties of the CZTS, with the first effect having the largest influence on device performance. The effect on CZTS can be difficult to determine given the normal spread in performance between devices.

David Mitzi enquired: There was mention in the presentation that aluminum oxide works better than hafnium or silicon oxides as a passivation layer when studying devices with Mo back contact. Also, the aluminum oxide in this part of the study was deposited by ALD rather than by sputtering (used for hafnium and silicon oxides). I was wondering whether the deposition process used (ALD *vs.* sputtering), and the associated impact on passivation layer morphology and continuity, might play a role in determining how well the different passivation layers work in improving the device performance?

Charlotte Platzer Björkman answered: There are two different experimental series in the paper, the first with sputtered SiO, sputtered Al_2O_3 and ALD Al_2O_3, and the second with ALD Al_2O_3 and ALD HfO. SEM cross-sections from the first series, with the thinnest passivation layers are shown in Fig. S1 in the ESI of the paper (https://doi.org/10.1039/d2fd00052k). There is no clear difference in the grain size or morphology in this case, also looking at the slightly thicker passivation layers (not shown). In the comparison of ALD HfO and Al_2O_3 (Fig. 5 of the paper), the CZTS grains are possibly larger for Al_2O_3 passivation, but the image is not clear enough to confirm this.

Susanne Siebentritt said: Al_2O_3 works better as a passivation layer not only in kesterites, but also in Si and in CIGS. This is because it not only passivates the contact, but it has negative charges that repel the electrons. See *e.g.* ref. 1 and references therein.

1 F. Werner, B. Veith-Wolf, C. Spindler, M. R. Barget, F. Babbe, J. Guillot, J. Schmidt and S. Siebentritt, *Phys. Rev. Appl.*, 2020, **13**, 054004, DOI: **10.1103/PhysRevApplied.13.054004**.

Charlotte Platzer Björkman responded: Thank you for the reference. Indeed, Al_2O_3 has been shown to work very well in Si and CIGS. In the studies of HfO_2 for Si and CIGS both positive and negative charge is reported (higher density of negative charges for HfO_2 compared to Al_2O_3, but better interface trap passivation for Al_2O_3 reported in ref. 1; positive charge in HfO_2 reported in ref. 2).

1 R. Scaffidi *et al.*, *Phys. Status Solidi A*, 2021, **218**, 2100073, DOI: **10.1002/pssa.202100073**.
2 H. Geng *et al.*, *Appl. Phys. Lett.*, 2014, **105**, 123905, DOI: **10.1063/1.4896619**.

Rafael Jaramillo asked: What specifically do you think is the passivation process, taking into account the physical intermixing that must happen during processing. Can you identify the presence of the passivation layer after processing, *e.g.* through microscopy cross sections?

Charlotte Platzer Björkman replied: We do see evidence of the passivation layer remaining after processing in the form of Al or Si signals at the interface by glow discharge optical emission spectroscopy (GDOES). In SEM cross-sections the layers are hard to see, TEM would be needed, but we do see reduced formation of MoS_2 in these cross-sections when passivation layers are added. The passivation process could be electrical, *i.e.* reducing electron flow from the absorber to recombination at the back contact through the wide band gap dielectric film, possibly supported by fixed charge in the oxide further repelling electrons. There could also be a beneficial chemical effect from reducing loss of S from the absorber in the anneal to MoS_2 formation, that might be beneficial for the absorber quality.

Devendra Tiwari said: This comment arises from the data presented by Professor Platzer Björkman on the effects of sodium fluoride layer deposition before and after low thickness (<750 nm) CZTS absorber deposition. The thin absorbers were grown on Mo or ITO coated glass substrates with alumina, silica and hafnia protective overlayers (<10 nm thickness). Upon reading further the earlier papers reported by Professors Platzer Björkman and Edoff from the Ångström Lab on related work on chalcopyrite and kesterite like compound Cu-chalcogenide absorbers (most importantly – ref. 1 and 2), and multiple reviews and studies on the role of alkali salts inclusion in such absorbers-based PV devices especially ref. 3 and 4, it is understood that different microscopic effects have been proposed to be prevalent for different alkali metals. For example, including intragrain improvement in carrier concentration and grain growth, and modulation of the intergrain barrier affecting the charge separation and transport. The observation of different effects for different alkali metal ions suggests multiple underlying mechanisms at play, for example changes in the ionic radii and electropositivity could affect the uptake of a particular alkali metal, *i.e.* whether it may substitute the sites in the crystallite or segregate at grain boundaries, and thermodynamic stability and the bonding nature of alkali metal based secondary phases, under a certain set of processing conditions. However, I am not sure whether it is due to historic or scientific reasons why prevalently fluorides of alkali metals have been employed to introduce alkali metals in the absorber especially when vacuum processing has been used and that the role of the fluoride anion has been discounted. In my view, fluoride being such a strong Lewis acid must participate in modifying the absorber films or absorber/buffer interface. Particularly in this paper (**https://doi.org/10.1039/d2fd00052k**), the authors observed improvements in the device performance for both the cases when NaF treatment was included before and after the precursor deposition. Thus, in both cases it could be inferred that NaF must have been acting on the protective oxide layers. The purpose of the stable and ultrathin conformal oxide protective layers has been to minimize the excess diffusion of chalcogens or metals across the back contact and introduce non-ohmic character to the charge-transport. However, such stable oxide layers of aluminium, silicon or hafnium are insulating and thus have been tested as gate-materials in FET devices and as a consequence in current PV devices of kesterite or chalcopyrite absorbers,[5] thus leading to s-kink + cross-over (Fig. 4a in the paper) or mild roll-over (Fig. 4b in the paper) in the J–V curves due to blocked charge transport. As shown in the previous papers,[5,6] addition of NaF leads to perforation of these oxide protective layers (*cf.* Fig. 5 of ref. 5) thus allowing charge-transport. My suggestion is that mechanistically, the fluoride must play a role in the partial erosion of the oxide of the protective layer, gettering any residual oxides at grain boundaries and should be investigated. The fluoride chemistry involved here is very basic and most of the work on the thermochemistry of such reactions involving the native oxide of simple metals and alkali salts predates the advances in the opto-electronic devices. However, there is colloquial evidence and two areas which might of relevance here including the role of fluoride chemistry in the etching of silica for FET devices and corrosion of native oxides of metals under fluoride solutions. Fluoride has been known to attack oxides, for example the RCA rinses include diluted HF treatment at the end step to etch SiO_2 on Si wafers (for example ref. 7) and similarly the fluoride content in water has been known to attack air-formed oxide on aluminium surfaces (*i.e.* alumina), for example see ref. 8, where the activity of NaCl and NaF have been compared and the latter has been found to be much more corrosive. The activity of fluoride towards such oxide has been known to be aggressive and isotropic. Various patents and studies have been reported to control the fluoride-based etching for FET devices. Similar observations of difficulty in controlling the etching of HfO_2 *vs.* Al_2O_3 with the action of a NaF overlayer was observed in ref. 5. Interestingly, in this work as well, the NaF layer deposited directly on top of the protective oxide layer resulted in worse performance compared to NaF deposited on the thin absorber precursor layer. The latter situation perhaps leads to a better control of fluoride release to the protective oxide layer, with likely transports through the grain-boundaries *via* adducts with any oxides or low coordination sites. Thus, it might be interesting as a further work to analyse the fluorine/fluoride/oxy-fluoride concentration across the device as a way of understanding the chemical mechanism of the fluoride-led oxygen/oxide etching. Of course, a reliable detection of fluorine or fluorine-species under such a low concentration with spatial resolution is difficult. However, as a suggestion use of low to medium energy ion spectroscopy could be a possibility. Fortunately, the authors have ERDA based ion-spectroscopy available to them. Lastly, the observed difference in the performance of devices with NaF and HfO_2 *vs.* Al_2O_3 could be again due to the differential fluoride ion affinity (FIA) as has been reported in gas-phase with Hf having a lower FIA than Al.[9,10] As a result, Fig. 5 of ref. 5 also shows less perforation for HfO_2 than Al_2O_3 of the same 15 nm thickness upon NaF treatment. Assuming similar behaviour, the differences in the *J–V* curves between Al_2O_3 and HfO_2 based devices in Fig. 4c of the paper can be explained by the presence of a more intact layer of HfO_2 blocking the charge transport. I recently came across this article which could be directly relevant to this discussion. Particularly, Deep Reactive Ion Etching Bosch process on Al_2O_3 for microelectromechanical device fabrication seems to have probed this issue in more detail. Its 2022 article, so includes in-depth and more refined surface analysis of erosion of Al_2O_3 under fluoride ion plasma (ref. 11).

1 S. Englund, V. Paneta, D. Primetzhofer, Y. Ren, O. Donzel-Gargand, J. K. Larsen, J. J. S. Scragg and C. Platzer Björkman, *Thin Solid Films*, 2017, **639**, 91.
2 D. Ledinek, J. Keller, C. Hägglund, W.-C. Chen and M. Edoff, *Thin Solid Films*, 2019, **683**, 156–164.
3 S. Siebentritt *et al.*, *Adv. Energy Mater.*, 2020, **10**, 1903752.
4 M. Krause, J. A. Márquez, S. Levcenco, T. Unold, O. Donzel-Gargand, M. Edoff and D. Abou-Ras, *Prog. Photovoltaics*, 2022, **30**, 109–115.
5 D. Ledinek, O. Donzel-Gargand, M. Sköld, J. Keller and M. Edoff, *Sol. Energy Mater. Sol. Cells*, 2018, **187**, 160 (ref. 15 in the paper).
6 S. Englund, V. Paneta, D. Primetzhofer, Y. Ren, O. Donzel-Gargand, J. K. Larsen and C. Platzer Björkman, *Thin Solid Films*, 2017, **639**, 91 (ref. 14 in the paper).
7 C. Ràfols, K. Herodes, J. L. Beltrán, E. Bosch and M. Rosés, *J. Electroanal. Chem.*, 1997, **433**, 77–83.
8 K. F. Lorking and J. E. O. Mayne, *Br. Corros. J.*, 1966, **1**(5), 181–182.
9 M. O'Keeffe, *J. Am. Chem. Soc.*, 1986, **108**(15), 4341–4343.
10 M. I. Nikitin, I. D. Sorokin, E. V. Skokan and L. N. Sidorov, *Russ. J. Phys. Chem.*, 1980, **54**.
11 M. Drost, S. Marschmeyer, M. Fraschke, O. Fursenko, F. Bärwolf, I. Costina, M. Kalishettyhalli Mahadevaiah and M. Lisker, *Micro Nano Eng.*, 2022, **14**, 100102.

Charlotte Platzer Björkman responded: Thank you for the comment. Indeed, probing the fluorine concentration profiles would be valuable.

Mirjana Dimitrievska asked: Have you looked into how the transmission and absorption of the thin films changes with the changes in the thickness of the films? How thin can you actually go with kesterites and still keep most of the beneficial properties?

Charlotte Platzer Björkman answered: We did not perform optical measurements for this set of samples and did not process them on transparent substrates (without Mo). However, we did study optical properties in ref. 1 and for CZTSSe in ref. 2 using ellipsometry, spectrometry and *ab initio* calculations, with and without polishing the surfaces. The CZTS samples in these studies were 500 and 800 nm thick. We have not tried to decrease the absorber thickness below 250 nm yet.

1 S.-Y. Li *et al.*, *Sol. Energy Mater.*, 2016, **149**, 170–178.
2 S.-Y. Li *et al.*, *Appl. Phys. Lett.*, 2017, **110**, 021905.

Thomas Weiss enquired: Concerning the devices with oxide layer at the back contact, do these oxide layers act as a barrier for alkali diffusion from the soda lime glass substrate? Have you ever checked the sodium content in your absorber films? Or more specifically: did you check the doping in your absorber layers with and without oxide layer at the back contact?

The reason is that Cu(In,Ga)Se_2, devices prepared without Na have a very high doping, which can lead to a back contact barrier. Summing up: the low device performance and the blocking of the diode current could be a result of lacking Na(/doping).

Charlotte Platzer Björkman responded: We did perform GDOES depth profiles of the samples with varying thickness of ALD Al_2O_3, sputtered Al_2O_3 and sputtered SiO on Mo and ITO. The estimated thicknesses were between 1 and 8 nm in this series. We did not see any difference in the Na concentration in the CZTS between these samples including the Mo and ITO references. The main difference in Na profiles between the samples was an accumulation of Na at the ITO/passivation layer interfaces that increased with increasing passivation layer thickness. We were expecting some blocking of Na, but reports on non-blocking barrier layers are not uncommon.

We have previously seen that TiN adhesion layers on Mo can actually increase the Na concentration in CZTS.[1] In that case we identified Na accumulation in the TiN and non-uniformities in the sputtered TiN on the Mo where Na could possibly pass. We also noticed strong reduction in MoS_2 formation, and this could also influence the Na supply to the CZTS from SLG since MoS_2 can block Na diffusion.

1 S. Englund *et al.*, *Thin Solid Films*, 2017, **639**, 91–97, DOI: 10.1016/j.tsf.2017.08.030.

Jens Wenzel Andreasen asked: We assume that morphology affects performance. Do you have any suggestions on ways to extend the modelling of photovoltaic performance to 3D, including a proper morphology representation?

Charlotte Platzer Björkman replied: There is literature on 3D modelling of solar cells as well as 2D modeling using for example Sentaurus TCAD. However, the challenge is to find accurate parameters for the modelling, something which is already hard in 1D characterisation and modelling.

Theodore Hobson queried: As a general question, where do you see this work going next? As in, what techniques might you employ to better analyse what seems to be conductive behaviour in the passivation layers? Could you see, for instance, photoemission being useful for probing the changing chemical and electrical characteristics of the layers?

Charlotte Platzer Björkman responded: Further characterisation of possible Na or F concentration within the passivation materials, including using thicker films to facilitate characterisation would be useful. Maybe exaggerated NaF treatments with TEM analysis could also help separate between possible explanations.

Jake Bowers asked: In the paper you grew some CZTS films on ITO substrates and saw some indium diffusion into the film. The ITO was deposited at room temperature. Did you try increasing the deposition temperature of the ITO to try and promote a more stable film which would not diffuse into the CZTS?

Charlotte Platzer Björkman replied: Thank you for the suggestion, no we did not try that.

Devendra Tiwari opened discussion of the paper by Galina Gurieva: Dr Gurieva presented crystallographic analysis of the $Cu_2(Zn,Mn)SnSe_4$ mixture through neutron and X-ray diffraction. Needless to say, the presented analysis is exemplarily systematic and thorough. However, inclusion of a mid-transition series element (*i.e.* non d^1 or d^9 ion) in a PV absorber raises concern, as such metal ions including Mn^{n+} do exhibit multiple oxidation states easily forming the basis for their use in catalysis. This in the case of a PV absorber could lead to undesired electronic states in the bandgap. Thus, it is critical to confirm the chemical state of the Mn ion in the samples. The similar scattering lengths of Mn in say +2 or +3 do not allow resolution of changes in the chemical state. It is noted that the average stoichiometry obtained from the crystallographic site occupancies deduced from refinement of diffractograms does indicate Mn in the intended +2 state. However, it cannot be considered as sufficient evidence of constancy of the chemical state of Mn throughout the sample given possibilities of the existence of Sn and Cu in compensating chemical states or disproportionation of the Mn state throughout the sample.

Thus, as future work, a suggestion is made to look at the magnetic structure of these mixture to indirectly elucidate the chemical state of magnetic ion Mn. Another suggestion could be to do an analysis of the real-space representation of the diffractogram to note any changes in the coordination or the internal coordinates of bond-lengths and -angles. Otherwise as a last resort, perhaps additionally use X-ray absorption spectroscopy and X-ray photoelectron spectroscopy to directly infer the chemical state of Mn in the bulk or at the surface.

Galina Gurieva responded: I would like to thank Dr Tiwari for this very extensive list of suggestions for checking the oxidation state of Mn. We will consider the possibility of performing one of the mentioned studies in the future. With regards to the suggestion to look at the magnetic structure of the mixture to indirectly elucidate the chemical state of the magnetic ion Mn, these mixtures show spin-ice behaviour at room temperature and thus such an analysis will be inconclusive for determining changes in the Mn chemical state.

Jonathan J. S. Scragg asked: Is your thesis that the stannite structure itself is somehow preventing disorder from occurring? Or is it instead to say that whichever features of a compound cause it to crystallise as stannite, also favour ordered material? *E.g.* a compound with similarly sized atoms – such as copper and zinc – might preferentially form a kesterite due to that size similarity, and for the same reason also be disordered. With atoms having larger size differences, stannite might be the preferred structure due to ion packing considerations, and the size difference also disfavours disorder. Is it that stannite prevents disorder, or that compounds that form stannite are inherently just not disordered?

Galina Gurieva answered: We differentiate 2 different types of disorder:

(i) the off-stoichiometry type related defects (for details please see ref. 1).

(ii) the Cu/Zn disorder, which is defined as equal amounts of Cu_{Zn} and Zn_{Cu} anti sites on the 2*c* and 2*d* cation sites in the kesterite type structure. The stannite type structure does not have 2*c* and 2*d* sites, it has 4*d*, which according to the definition is occupied exclusively by Cu.

1 S. Schorr, G. Gurieva, M. Guc, M. Dimitrievska, A. Pérez-Rodríguez, V. Izquierdo-Roca, C. S. Schnohr, J. Kim, W. Jo and J. M. Merino, *JPhys Energy*, 2020, **2**, 012002, DOI: 10.1088/2515-7655/ab4a25.

Jonathan J. S. Scragg said: You noted that the stannite structure places Zn/Mn and Cu into different planes, which could be the reason that disorder is not observed, *i.e.* that intraplane disorder is "easier" than interplane disorder. This seems surprising – exchanging atoms between planes, especially in the case of a vacancy or interstitial assisted process, does not seem like it should require a high energy, *i.e.* it could occur for materials synthesised at high temperature. Could you say anything about the "barrier" that you think stannite induces, maybe with reference to some other literature (*e.g.* in another system)?

Galina Gurieva responded: The stannite structure does give the possibility for Cu/Zn disorder as it doesn't have the 2*c* and 2*d* cation sites, it has 4*d* only, which is occupied by Cu. The interplane disorder could be described by disorder in a different plane, *e.g.* in the plane {100}, but it is not found experimentally.

Jonathan J. S. Scragg asked: Is there much difference in the formation energy of Cu–Zn antisites in stannite with respect to kesterite?

Galina Gurieva replied: There is no experimental evidence for Cu/Zn disorder in stannite type materials.

David Scanlon enquired: I am wondering why Mn was chosen as the dopant to reduce the disorder in this system. Mn is a transition metal, and in the 2+ oxidation state, are the localized d states that may form in the band gap or near the band edges going to be more detrimental than the effect of removing the disorder?

Galina Gurieva answered: Our motivation was the study of structural cross-over from kesterite to stannite while reaching for a very interesting bandgap range. CMZTSSe thin film solar cells, prepared by chemical spray-pyrolysis and a subsequent selenization process were studied recently. The best photovoltaic device is obtained with the sample with Mn content of 0.05 with improvements in the depletion width, V_{oc}, and fill factor.[1]

1 S. Lie, J. M. Rui Tan, W. Li, S. W. Leow, Y. F. Tay, D. M. Bishop, O. Gunawan and L. H. Wong, *J. Mater. Chem. A*, 2018, **6**, 1540–1550, DOI: 10.1039/c7ta09668b.

David Scanlon asked: Has anyone done any DFT calculations to understand what happens to the electronic structure when someone dopes Mn into this system?

Galina Gurieva responded: Quite a few DFT calculations were done on Mn doped systems: *e.g.* ref. 1 and 2 for Cu_2MnSnS_4, or $Cu_2Cd_{1-x}Mn_xSnSe_4$ (ref. 3) but unfortunately we are not aware of DFT calculations done for $Cu_2Zn_{1-x}Mn_xSnSe_4$.

1 K. Rudisch, W. F. Espinosa-García, J. M. Osorio-Guillén, C. M. Araujo, C. Platzer-Björkman and J. J. S. Scragg, *Phys. Status Solidi B*, 2019, **256**, 1800743, DOI: 10.1002/pssb.201800743.
2 R. Chen and C. Persson, *J. Appl. Phys.*, 2017, **121**, 203104, DOI: 10.1063/1.4984115.
3 F. S. Liu, J. X. Zheng, M. J. Huang, L. P. He, W. Q. Ao, F. Pan and J. Q. Li, *Sci. Rep.*, 2014, **4**, 5774, DOI: 10.1038/srep05774.

David Fermin enquired: This is a beautifully conducted piece of research. Could you rationalize cation ordering and changes in band gap in terms of bonding characteristics? For example, could the trends seen in Fig. 3 and 9 of the paper (**https://doi.org/10.1039/d2fd00042c**) be the result of an interplay between geometric (ionic radii) and electronic effects (bond strength) upon replacing Zn^{2+} by Mn^{2+}?

Galina Gurieva replied: The atomic arrangement in crystal structures is always a result of interplay of geometric (ionic radii) and electronic (bond strength) effects (and maybe more). The trends seen in Fig. 3 and 9 of the paper (**https://doi.org/10.1039/d2fd00042c**) could be the result of such processes.

Kostiantyn Sopiha requested: Could you comment on the magnetic state of $Cu_2MnSnSe_4$ at low temperatures? Is it ferromagnetic? This could be critical if the results are to be cross-correlated with DFT (if not done already).

Galina Gurieva answered: The magnetic state reported for $Cu_2MnSnSe_4$ was spin-glass with a freezing temperature T_f of about 22 K and Curie–Weiss temperature $\theta = -25$ K.[1] There are also some old reports showing the antiferromagnetic behaviour for this compound.[2] If the material is antiferromagnetic at room temperature, we would observe additional peaks in the neutron diffraction patterns, which is not the case.

1 E. Quintero, M. Quintero, E. Moreno, L. Lara, M. Morocoima, F. Pineda, P. Grima, R. Tovar, P. Bocaranda, J. A. Henao and M. A. Macías, *J. Phys. Chem. Solids*, 2010, **71**, 993–998, DOI: 10.1016/j.jpcs.2010.04.010.
2 X. L. Chen, A.-M. Lamarche, G. Lamarche and J. C. Woolley, *J. Magn. Magn. Mater.*, 1993, **118**, 119–128, DOI: 10.1016/0304-8853(93)90165-X.

Rachel Woods-Robinson questioned: We have been discussing “ordering” as it refers to cation arrangement in a lattice, but should we consider magnetic order and disorder as another axis here? It has been reported for other semiconductors with magnetic cations that the magnetic ordering influences optical and electronic properties, such as VBM dispersion[1] and electronic conductivity,[2] and in other cases it has been reported that off-stoichiometry induces changes in magnetic ordering.[3] Therefore, would you expect that tunable properties in $Cu_2Zn_{1-x}Mn_xSnSe_4$, such as cation off-stoichiometry or cation order–disorder ratio, impact whether the material is a spin glass or starts to have some onset of magnetic ordering? If so, how would you expect that to impact the material's optoelectronic properties?

1 S. Mandal *et al.*, *Phys. Rev. B*, 2019, **100**(24), 245109.
2 K. Jindal *et al.*, *Mater. Today: Proc.*, 2021, **47**, 1637–1640.
3 B. Idzikowski *et al.*, *J. Alloys Compd.*, 2006, **423**(1–2), 267–273.

Galina Gurieva responded: We agree that magnetic order and disorder is a very important topic indeed. But experimentally, using neutron powder diffraction, we did not observe any magnetic behavior in our materials.

Thomas Weiss enquired: You determine the neutron scattering length experimentally. By how much are these derived values dependent on vacancies (*i.e.* V_{Cu})?

Even though you state in the paper (https://doi.org/10.1039/d2fd00042c) that no vacancies are anticipated, there could still be a small amount of vacancies present (below the detection limit of the compositional measurement). By how much would these vacancies influence the derived neutron scattering lengths?

Galina Gurieva replied: We do determine the average neutron scattering length of each of the cation sites by multiplying the neutron scattering length of the element we expect on this site with the site occupancy factor we obtain from the refinements (see more about the method in ref. 1). The derived values do depend on the vacancies but the amount of vacancies below the detection limit of the compositional measurement (less than 1%) would not affect the average neutron scattering length significantly.

1 S. Schorr *et al.*, X-ray and neutron diffraction on materials for thin-film solar cells, in *Advanced Characterization Techniques for Thin Film Solar Cells*, ed. D. Abou-Ras, T. Kirchartz and U. Rau, Wiley-VCH Verlag GmbH and Co. KGaA, 2011, p. 347.

Thomas Weiss asked: How can you distinguish manganese on copper in light of the possibility for the presence of copper vacancies?

Galina Gurieva answered: Manganese has a negative neutron scattering length, even 1% manganese on the copper site is reducing the average neutron scattering length of this site significantly. For example, the 2*a* position would give the following values of average neutron scattering length: 100% Cu = 7.718(10) fm, 99% Cu + 1% V_{Cu} = 7.641(10) fm, 99% Cu + 1% Mn = 7.603(10) fm, the error is estimated based on a typical experimental error from the refinement. In this way it is clear the effect of Mn is almost twice as strong as the one from vacancies.

Thomas Weiss enquired: In Fig. 8 of the paper (https://doi.org/10.1039/d2fd00042c) you present that you have a considerable amount of interstitial point-defects present. How do these defects influence the neutron scattering lengths?

These defects would need to be taken into account in the compositional analysis. In other words: if the site-occupancies are calculated according to the algorithm defined by eqn (3) and (4) of the paper, does any interstitial defect need to be compensated by a vacancy defect? Thus, the neutron scattering lengths are altered by these defects?

Galina Gurieva replied: We establish the cation distribution model considering the cation sites of the kesterite and stannite structures (2*a*, 2*c*, 2*d* and 2*b*) and (2*a*, 4*d* and 2*b*) respectively. Interstitials do not correspond to those sites. The neutron scattering lengths of the cation sites according to the kesterite type structure are not altered by interstitials, as interstitials are not located on those sites. We could probably observe some effect on the diffraction pattern if interstitials were ordered in a certain position in the unit cell, but as the distribution is random, no effect on the diffraction pattern is observed either (for possibility of the effect on the diffraction pattern in the case of ordering, please see ref. 1).

1 K. Neldner, Structural trends and phase relations in off-stoichiometric kesterite type compound semiconductors, Dr. rer. nat. dissertation, Freie Universität Berlin, 2017, DOI: **10.17169/refubium-13976**.

Rafael Jaramillo questioned: Is there a model of endotaxy or ordered secondary phases that could be hiding in your matrix that could be responsible for the fact that the band gap seems to be independent of composition?

Galina Gurieva responded: The bandgaps of the secondary phases, which could be hiding in the matrix and wouldn't be detectable by WDX, would be wider than the ones of the quaternary compounds (*e.g.* MnSe). That would make their influence very improbable.

Seán R. Kavanagh asked: In Fig. 9 of the paper (**https://doi.org/10.1039/d2fd00042c**), you show the bandgap is quite insensitive to both disorder and the $Zn_{(1-x)}Mn_x$ ratio, all the way up to $x = 0.7$, at which point it changes from kesterite to the stannite structure and suddenly there's a strong correlation between order/disorder and the Zn/Mn ratio. This insensitivity to order/disorder and Zn/Mn ratio for $x < 0.7$ seems possibly related to the low zinc contribution to the band edge, mentioned in the discussion of the previous paper. Do you think the large change in the bandgap for $x > 0.7$ could be an indirect effect of lattice strain in this composition range, as you report a much more rapid change in the lattice parameters in this range (Fig. 3 of the paper)?

Galina Gurieva replied: In alloyed systems, if the structure doesn't change we expect bowing behavior. Such a behavior can be seen in the areas of 0–20% manganese and 70–100% manganese. The re-distribution process happening between 20 and 70% manganese leads to very high disorder in 2*a*, 2*c* and 2*d* cation sites. As a result in this range the bandgap stays almost constant. The tail states due to disorder have a strong influence as well.

Joachim Breternitz opened discussion of the paper by Matthew Naylor: Was an internal standard used for the determination of the crystallite size using the Scherrer equation to consider the instrumental broadening of the diffractometer?

Matthew Naylor replied: No internal standard was used. Instead, the standard factor found in literature was used as an approximation.

Joachim Breternitz commented: If the instrumental broadening was not considered, the values given are probably an underestimation of the real crystal size. Taking an instrumental broadening of 0.06° on the full-width at half maximum (FWHM) into account in a back-of-an-envelope calculation, the calculated size using the Scherrer equation would change from 88 nm to over 200 nm.

Joachim Breternitz asked: The crystallite sizes are relatively large given you start from nanoparticles. Does that mean the particles fuse in some way during the thin film formation?

Matthew Naylor responded: Yes, the nanocrystals undergo a growth process facilitated by a S–Se chalcogen exchange process. You can read in detail about how this mechanism takes place in our previous work.[1,2]

1 Y. Qu, G. Zoppi and N. S. Beattie, *Sol. Energy Mater. Sol. Cells*, 2016, **158**, 130–137, DOI: **10.1016/j.solmat.2015.12.016**.
2 Y. Qu, S. W. Chee, M. Duchamp, S. Campbell, G. Zoppi, V. Barrioz, Y. Giret, T. J. Penfold, A. Chaturvedi, U. Mirsaidov and N. S. Beattie, *ACS Appl. Energy Mater.*, 2020, **3**, 122–128, DOI: **10.1021/acsaem.9b01732**.

Matias Valdes questioned: You have used 50 nm of Ge and you said that this could maybe be even higher. Normally the Ge amount is quite low, around 5 and 20 nm. Could you please elaborate more on this issue?

Matthew Naylor answered: In this study we use highly crystalline nanoparticles, so-called nanocrystals, which we believe adds a degree of selectivity with respect to Ge doping and Ge inclusion. Therefore, 50 nm of Ge was used as an upper range to probe possible effects of Ge incorporations in a precursor of such *crystalline* nature. The relationship between precursor crystallinity and acceptance of dopant elements has been sparsely investigated for CZTS and CZTSSe films. Nevertheless, this work resides in line with reports in the literature that suggest highly crystalline sample are less receptive of dopant elements (for example reports see: ref. 1). The significance of this work is the application of this trend to decouple Ge doping/alloying effects from wider Ge incorporation effects. Thank you for raising this point of discussion. A concise review by the kesterite community comparing elemental incorporations as appose to isoelectric substitutions could be a useful addition to the literature.

1 M. Neuschitzer, J. Marquez, S. Giraldo, M. Dimitrievska, M. Placidi, I. Forbes, V. Izquierdo-Roca, A. Pérez-Rodriguez and E. Saucedo, *J. Phys. Chem. C*, 2016, **120**, 9661–9670, DOI: **10.1021/acs.jpcc.6b02315**.

Charles J. Hages asked: There is almost 40% Ge/Sn in the final film (for the largest Ge concentration). Ge shows incorporation into the bulk structure based on XRD and Raman shifts. So, if Ge is alloyed into the film, why doesn't the bandgap shift in any of your films?

Matthew Naylor replied: This is a good train of thought. In the paper (**https://doi.org/10.1039/d2fd00069e**) we distinguish between Ge-doping (low level) and alloying (high level). This ratio does not match the XRD/Raman shifts which leads us to conclude that Ge is acting as a crystallisation aid. This is likely also the reason why only marginal energy bandgap shifts are observed.

Charles J. Hages enquired: Have you compared the measured shift in XRD peak location (according to Vegard's law) with the measured Ge-content in the films? What is the expected alloying of Ge/Sn based on this XRD peak shift?

Matthew Naylor responded: This is a good suggestion. As the focus of this study was Ge-doping as opposed to Ge-alloying XRD analysis was initially undertaken to investigate other phases but we will take this suggestion forward, although I suspect further refinement will be needed due to the small shift angles.

Charles J. Hages queried: It is surprising that you don't see a bandgap shift if the Ge/Sn alloy is showing up in composition measurements, XRD, and Raman. It is possible there is a Ge-gradient in the film since these nanoparticles and added germanium completely recrystallize upon selenization. Would a Ge gradient be causing a challenge to measure the optical properties at various Ge concentrations?

Matthew Naylor replied: This topic of recrystallisation is not well established in the literature and makes a good point for discussion. The effect of initial crystallinity of the nanocrystals (and metallic stacks also) is found to add a degree of selectiveness (with respect to accepted *ex situ* doping routes) – there is no such reason for this established in literature at present.

Yes, we believe there is a slight Ge-gradient towards the rear of the film (the original location of Ge) which indeed makes optical measurements complex. For future studies, the community should perhaps delaminate the $MoSe_2$/CZTSSe interface and study properties of the rear surface. It would be beneficial to have an accepted procedure for this in the community so rear film damage is consistent across research centres. Thank you for this insightful discussion.

Susan Schorr asked: In the structural analysis you have used XRD data and here especially the peak shift and width of the 002 Bragg peak. Why you have used the 002 Bragg peak for this analysis? This peak is one of the smallest Bragg peaks in the XRD pattern (relative intensity of 0.4 to 1.2% assuming for the 112 Bragg peak with 100%). Why have you not chosen the 112 peak for that analysis?

Also, shifts of Bragg peaks due to incorporation of other elements into the crystal structure become more pronounced at higher 2θ values. But the 002 Bragg peak appears at quite low 2θ (15.6 to 15.7°). In my opinion the 002 Bragg peak is not very suitable for the analysis you have performed. Again, why you have not chosen the strongest peak, the 112 Bragg peak?

Matthew Naylor answered: Thank you for the comments. Yes, I agree this is not the conventional route for this type of analysis. The role the crystallite size in this study was to qualitatively show increased crystal growth and as such the general validity remains. With hindsight, methods such as the Williamson–Hall plot would have elevated this issue. Thank you for raising this point of discussion.

Mirjana Dimitrievska said: Regarding the shift in the A mode ($199\ cm^{-1}$) in the Raman spectra towards higher cm^{-1}. It has been shown that this shift occurs when the S/Se ration also changes (films become more S-rich).[1] You are claiming that this shift proves the incorporation of Ge into the films, but how can you decouple the changes in the anion ration from the changes in Ge concentration, when both would essentially lead to the same shift? One way might be to check the S-like peak at around 330 cm^{-1}. If it is the case there are no changes in the position of this peak, then I would assume that indeed the shift of the peak at 199 cm^{-1} is related to Ge incorporation.

1 M. Dimitrievska, G. Gurieva, H. Xie, A. Carrete, A. Cabot, E. Saucedo, A. Pérez-Rodríguez, S. Schorr and V. Izquierdo-Roca, *J. Alloys Compd.*, 2015, **628**, 464–470, DOI: 10.1016/j.jallcom.2014.12.175.

Matthew Naylor responded: This is an insightful line of discussion indeed. For this study the emphasis was to investigate the effects of doping as appose to alloying and as such the reported Raman shifts are relatively small. As you identified in the question it is important to decouple contributors to a Raman shift especially in a quaternary system. In this regard, yes but S/Se and Sn/Ge may both be contributing to an increased shift in the A mode (199 cm^{-1}) peak, comparing the literature provided and a reference for Sn/Ge, see ref. 1. As the selenisation process was measured consistent between samples it is reasonable to assume that Ge-incorporation is primarily responsible for this change, but to claim this exclusively further investigation would be necessary. Ultimately Raman measurements were undertaken to confirm phase purity as appose to quantify the amount of substitution. This discussion possibly mandates the need new rule-of-thumb for Raman analysis for better data completeness in literature. Thank you again for the discussion.

1 M. Grossberg, K. Timmo, T. Raadik, E. Kärber, V. Mikli and J. Krustok, *Thin Solid Films*, 2015, **582**, 176–179, DOI: 10.1016/j.tsf.2014.10.055.

Mirjana Dimitrievska asked: How do you calculate the "asymmetry" of peaks in the Raman spectra?

Matthew Naylor answered: Asymmetry may be calculated using a variety of fitting models. One such model is Bigaussian.

Mirjana Dimitrievska enquired: Have you also looked at the changes in the width of the Raman peaks?

Matthew Naylor replied: Thank you for raising this point of discussion. Yes, this property was studied from an asymmetric point of view. For these cases of Ge doping the property of peak widths was not reported on in detail but a future study on Ge alloying would merit a detailed investigation into any change to this property.

Jens Wenzel Andreasen queried: I did not quite understand how you distinguish between *ex situ* and *in situ* incorporation of Ge and how this is coupled with the distinction between alloying and doping. Could you explain what you mean by that?

Matthew Naylor answered: This distinction was implied to better place this study in densely published topic. In general most *in situ* routes (*i.e.* Ge introduced as the precursor is formed) can be said to generally represent Ge-alloying as the incorporation of Ge is often over a few atomic%. In contrast *ex situ* routes (*i.e.* after the precursor is formed) can be said to generally represent doping as the incorporation of Ge is generally less than 1 atomic%.

Incorporation in this instance is used to describe the transition of Ge source into a CZTS or CZTSSe film.

Jens Wenzel Andreasen asked: Follow up to the previous question: I am still not sure what you mean by *ex situ* and *in situ*, could you elaborate?

Matthew Naylor replied: In addition to the previous response please see ref. 1 and 2 below which add context to the *in situ*/*ex situ* convention. Once again this convention is not fully established in the literature but implied here to differentiate the multiple routes of Ge incorporation.[1,2]

1 Y. E. Romanyuk *et al.*, *JPhys Energy*, 2019, **1**, 044004, DOI: 10.1088/2515-7655/ab23bc. See Section 1 for a wider introduction into doping and alloying.
2 N. Benhaddou *et al.*, *J. Mater. Chem. C*, 2020, **8**, 4003, DOI: 10.1039/c9tc06728k. See Table 1 for a comparison of Ge doping and alloying quantities of Ge and also route of incorporation.

Phillip J. Dale queried: Looking at your scanning electron microscopy images, it looks like the carbon layer at the molybdenum interface is significantly smaller for the germanium containing kesterite. Is that correct, and does Ge play a role in catalysing carbon removal?

Matthew Naylor answered: This is a good observation and point for discussion. Multiple cross-section scanning electron microscope images were taken across the sample set and as such yes, we do think this reduction is correct. In terms of Ge playing a role in catalysing carbon removal, our opinion is along a similar but different line of thought. The fine grain layer in our devices is mainly comprised of residual carbon from the hot-injection process but does however contain a quantity of Se and S as well as traces of Cu, Zn and Sn. Building on the previous, it is possible that Ge assisted growth mechanisms allow for greater mass transport allowing for the traces of Cu, Zn and Sn to play an active role in the recrystallisation process.

Phillip J. Dale enquired: Do you have a hypothesis of how the germanium inclusion helps grain growth and makes a more compact carbon layer? For example does germanium selenide form a liquid phase?

Matthew Naylor replied: Our hypothesis of Ge-assisted grain growth is similar to that found in literature. Due to an elevated Se vapour pressure the reaction between Se and Ge forms highly Se compensated species such as Ge_3Se_7. As you said and in accordance with the Ge–Se phase diagram these types of species form liquid phases which can act as a flux to enhance mass transport. This enhanced flux decreased the likelihood for trace unreacted metallic species to be present in the carbon layer thus, decreased the thickness of the fine grain layer.

David Mitzi asked: With introduction of a Ge layer at the back of the CZTS precursor film during processing, better CZTSSe device properties are reported. I was wondering how the introduction of the Ge layer on top of the molybdenum substrate might impact the formation of molybdenum selenide during selenization and how these prospective differences in the $MoSe_2$ layer might contribute to changes in device performance? Is there any evidence of Ge–Mo alloying or compound formation at the back contact during the selenization process?

Matthew Naylor answered: This is an astute observation. We do not believe in this study that the presence of Ge adjacent to Mo forms Ge–Mo alloys and has little to no effect on the formation of $MoSe_2$. Regarding Ge–Mo alloys, crystallographically there is no evidence to suggest the formation of alloys but to rule out the existence of these species a dedicated GI-XRD and Raman study would need to be undertaken.

Regarding the formation of $MoSe_2$, the formation mechanism in our devices is heavily dictated by the properties of the Mo back contact films. These properties of the single Mo layer allow for reasonable conductivity while suppressing thickness of $MoSe_2$, such properties emanate from the deposition parameters of the DC sputtering process. Due to a suppressed $MoSe_2$ formation and the Ge diffusion towards the front of the device we surmise that Ge has little influence on the formation mechanism of $MoSe_2$.

A Ge-influenced mechanism might present itself however if the Mo properties were different and/or the selenisation conditions were elevated and/or prolonged. As you raised, the role of $MoSe_2$ is of a great importance to device performance.

Mingqing Wang questioned: Based on the XPS result, the surface of CZTS film in your work is very Zn poor, this will affect the photovoltaic performance of your device. Have you done any surface treatment to remove the extra binary or ternary phase contamination?

Matthew Naylor responded: This is a good observation. Typically CZTS(e) films are Zn-poor at the surface and Zn-rich towards the rear. In general, the literature supports this Zn gradient through the use of XPS, SIMS and or EDS depth profiles. A slight Zn gradient is observed in this work (**https://doi.org/10.1039/d2fd00069e**) but is not as prolific as the average literature case. This considerable composition change could indeed indicate segregation of CZTS quaternary nanocrystals into binary and ternary phases. In our experience starting with a quaternary precursor results in a benign segregation process. Nevertheless, surface treatments such as chemical etches would most likely compensate for this segregation to a degree. This study did not undertake any such surface treatments.

Jens Wenzel Andreasen addressed David Mitzi: You mentioned the unattractive properties of amorphous silicon which has prevented their proliferation. Can you elaborate on what those disadvantages are?

David Mitzi replied: Amorphous silicon (a-Si) was the dominant thin-film PV technology prior to the early 2000s. However, the amorphous (non-crystalline) nature and significant density of dangling bonds lead to substantial band tailing, a short minority carrier diffusion length and relatively inferior electrical transport properties. Also, the absorber performance degrades under light illumination (Staebler–Wronski effect). These factors opened an opportunity for chalcogenide absorber systems like CdTe and Cu(In,Ga)(S,Se)$_2$ (CIGS) to overtake a-Si after around 2005.

Susanne Siebentritt continued discussion of the paper by Galina Gurieva: You see complete Cu–Zn disorder as soon the Mn content is above 20%, as if Mn catalysed disorder. Do you understand what's happening there.

Galina Gurieva answered: 20% manganese is the point where the cation re-distribution process, which transfers the kesterite to stannite structure, starts. The 2*c* and 2*d* positions are occupied by 3 different cations at this point – Cu, Zn and Mn (Cu/II disorder). Thus the Q value goes down to 0. The situation stays constant until there are only 2 cations (Cu and Mn) left on the 4*d* site (former 2*c* and 2*d*) and the cation re-distribution process is over.

Charlotte Platzer Björkman enquired: I'm wondering about the cooling you used, what is meant by dynamic cooling? And did you try quenching or dis-ordering for the full Mn compound?

Galina Gurieva replied: With the dynamic cooling we mean a natural cooling, which is quite fast in the beginning (around 100 K h^{-1}) till 400 °C, and gets slower after – on average 50 K h^{-1} in the 400–250 °C range, and 10 K h^{-1} from 250 °C to room temperature.

We did not try quenching or disorder on the full Mn compound yet, but it would be a very interesting study for the future.

Thomas Weiss opened a general discussion: We have seen that “kesterites” (the kesterite family) can be alloyed with many different elements. With that it is possible to introduce bandgap gradients for surface passivation/charge collection and to reduce Cu–Zn disorder. However, what needs to be done to overcome the large V_{oc}-deficit?

David Fermin added: Can we reach a consensus on whether V_{oc} deficit in kesterite solar cells is connected to either Cu/Zn or Sn-related disorder, or some other defect?

Jonathan J. S. Scragg replied: My feeling is that the main part of the V_{oc} deficit is related to one or more deep defects (though these may not be simple point defects). Disorder is presumably a contribution but not the main contribution.

Susanne Siebentritt commented: The band tails in kesterites are not due to the Cu–Zn disorder. We can deliberately change the degree of order over a wide range by annealing, see ref. 1. But the Urbach energy does not change, neither does the V_{OC} deficit. For Urbach energy, see ref. 2; for V_{OC} deficit, see ref. 3.

1 G. Rey, A. Redinger, J. Sendler, T. P. Weiss, M. Thevenin, M. Guennou, B. El Adib and S. Siebentritt, *Appl. Phys. Lett.*, 2014, **105**, 112106, DOI: 10.1063/1.4896315.

2 G. Rey, G. Larramona, S. Bourdais, C. Choné, B. Delatouche, A. Jacob, G. Dennler and S. Siebentritt, *Sol. Energy Mater. Sol. Cells*, 2018, **179**, 142–151, DOI: **10.1016/j.solmat.2017.11.005**.

3 G. Rey, T. P. Weiss, J. Sendler, A. Finger, C. Spindler, F. Werner, M. Melchiorre, M. Hála, M. Guennou and S. Siebentritt, *Sol. Energy Mater. Sol. Cells*, 2016, **151**, 131–138, DOI: **10.1016/j.solmat.2016.02.014**.

David Mitzi responded: When we talk about disorder, I believe that this directly connects with defects, whether this refers to anti-sites, vacancies or interstitials. Overall, I think that anti-site disorder likely plays an important role in the V_{oc} deficit, even if Cu–Zn disorder may not be the dominant player. For example, as noted by others, Sn–Zn related defects may also be important in terms of recombination losses.

Mirjana Dimitrievska added: There is a very nice recent theoretical paper which proves this point exactly. To quote from their abstract: "…band-gap fluctuations contribute only marginally to the V_{OC} deficit, thereby excluding Cu–Zn disorder as the primary source of the low efficiency of CZTS devices. On the other hand, the extensive disorder stabilizes the formation of Sn_{Zn} antisite and its defect complexes, which as nonradiative recombination and minority carrier trapping centers dominate the V_{OC} loss in CZTS. Our analysis indicates that current CZTS devices might have already approached the maximum conversion efficiency (14%) given the limited growth conditions and the remnant cation disorder even after postannealing."[1]

1 W. Chen, D. Dahliah, G.-M. Rignanese and G. Hautier, *Energy Environ. Sci.*, 2021, **14**, 3567–3578, DOI: **10.1039/d1ee00260k**.

David Mitzi remarked: Even commercial CdTe until very recently also uniformly suffered from a large V_{oc} deficit – *e.g.*, V_{oc} = 887.2 mV (relative to a 1215 mV SQ limit for a band gap of 1.5 eV) in the record CdTe solar cell with 22.1% efficiency.[1] Relatively high performance in these devices is achieved by optimizing other aspects of the device performance, despite the substantial V_{oc} deficit. Recent demonstrations of high V_{oc} (>1000 mV) in CdTe devices has appeared in the literature by introducing group V doping.[2]. Nevertheless, these newer generation cells have not yet reached record power conversion efficiency levels.

1 M. A. Green, E. D. Dunlop, J. Hohl-Ebinger, M. Yoshita, N. Kopidakis, K. Bothe, D. Hinken, M. Rauer and X. Hao, Solar cell efficiency tables (Version 60), *Prog. Photovoltaics*, 2022, **30**, 687–701, DOI: **10.1002/pip.3595**.

2 J. M. Burst, J. N. Duenow, D. S. Albin *et al.*, CdTe solar cells with open-circuit voltage breaking the 1 V barrier, *Nat. Energy*, 2016, **1**, 16015, DOI: **10.1038/nenergy.2016.15**.

Jake Bowers commented: In terms of the V_{oc} deficit in CZTS films, some of the breakthroughs in the CdTe community (which for a long time suffered from V_{oc} not more than 850 mV) came from single crystal growth, which then developed into solar cells with V_{oc} of over 1 V. Perhaps the community can learn from monograin type devices, or again revisiting the growth of single crystals.

Charles J. Hages noted: Regarding the potential to fix the V_{oc} deficit in kesterites: our work in CZT(S,Se) has shown the material has recombination lifetimes on the order of hundreds of picoseconds. There is a lot more going on in the characterization data (*e.g.* TRPL) since they are non-ideal than is initially apparent or easily extracted. This doesn't really agree with shallow tailing problems that can be resolved with single crystals or order/disorder transitions; rather, there are significant deep defects that are intrinsic to the material itself that kill the lifetime.

Jonathan J. S. Scragg said: Defects are obviously critical, but I suspect we are not always looking in the right places for the defects we blame for our problems. In CZTS, we know there are deep Sn-related defects. Ge alloying is claimed to suppress these, which is a motivation for Ge alloying. I don't buy that argument: replacing 10% of the Sn atoms would not make enough of a difference to the concentration of deep Sn-related defects to matter for device performance. And yet, Ge inclusion does create some improvements. How does it do that? In another example, we saw that thinning the CZTS layers allowed performance to be retained surprisingly well. The common feature in both examples is that morphology is improved. I think we need to pay more attention to morphologically related defect structures – for example, dislocations, twins, planar defects, stacking faults *etc.*, that can occur in our crystals but which we really do not pay much attention to. What if such features contribute to band tailing, defect levels, *etc.* We need some better ways of evaluating crystal quality, to quantify the presence of structural defects and give us the means to investigate this hypothesis.

Thomas Unold responded: I think this is a good point. However we should always consider that in material of different quality there might be different reasons that limit recombination. In a recent study[1] in fact grain boundaries were identified to limit performance (to 12%) – which means that in these films the bulk point defects have been significantly reduced.

[1] J. Li, J. Huang, F. Ma *et al.*, Unveiling microscopic carrier loss mechanisms in 12% efficient $Cu_2ZnSnSe_4$ solar cells, *Nat. Energy*, 2022, 7, 754–764.

Matthew Sutton enquired: What are general opinions on approaching solar cell design from a stability-first or performance-first standpoint? I think performance-first is quite common, for example with perovskite cells, however ideally cells could be built from stable materials to begin with rather than the substitution/passivation currently needed for perovskites. Wondering what others' thoughts are on this.

Mirjana Dimitrievska replied: I think now, more and more researchers are considering both aspects equally, so we are on a good point moving forward.

Joachim Breternitz added: I believe this is an important point for the future and the prospect of designing materials that favour stability over performance at the first glance is pretty appealing. However, I have the feeling that we may face the problem – at least from an experimental point-of-view – that performance is much quicker to assess than stability (especially of devices). The latter may afford experiments that take much more time for each individual experiment and hence prolong this first assessment step significantly. I believe that due to this, a concentration on stability in the first instance appears more natural. It is, however, most important to bear all aspects in mind as they all play a role in a final assessment. Therefore, I would argue that both aspects, performance and stability, need to be considered at every stage.

Alex Ganose remarked: Typically the role of the effective mass of the absorber has been seen as a trade-off: small effective masses give high mobility but small joint density of states (JDOS) leading to poor absorption coefficients, whereas high effective masses give large JDOS and high absorption but poor mobility.

However, that is only for a single valley, single band model. There is a way to optimise both JDOS and effective masses by having a system with a high valley degeneracy. In this case, each valley can be very disperse (with a small effective mass) but the degeneracy (due to symmetry equivalent valleys throughout the Brillouin zone) can result in large JDOS. You typically find this behaviour in high-symmetry systems where the band edges occur away from a high-symmetry point in the Brillouin zone. This same design principle is widely used by the thermoelectrics community.

The valleys do not even have to be symmetry equivalent. For example, some emerging absorbers like Sb_2Se_3 and GeSe have many valence and conduction band pockets, some of which are quite disperse with small effective masses, but also have strong optical absorption.

Kostiantyn Sopiha addressed David Mitzi: You mentioned that Ag substitution in CZTS reduces hole density and converts the material into n-type, which complicates the potential device structure. What do you think about adding external dopants? Does it have the potential to keep Ag-alloyed CZTS p-type and hence stick with the same device structure? If yes, what dopants would you consider suitable (if you have any guesses)?

David Mitzi answered: This is a good question. Generally speaking, although intrinsic CZTS and CZTSe are p-type, the analogous Ag-substituted materials are n-type. The switch in carrier type occurs because of changes in the band structure and associated readily formed intrinsic defects (as described, for example, in ref. 1). While in principle, one can try to determine possible dopants to p-dope AZTS/AZTSe, in practice the process of doing this is likely to be complicated by compensation mechanisms – in other words, an impurity may be added to dope the semiconductor, but the resulting prospective shift in Fermi level will induce other defects to form that will counteract the doping effect of the impurity. Based on defect calculations, it is expected that p-type doping may be difficult in AZTS/AZTSSe. Nevertheless, there have been some reports of possible p-type conductivity in these systems (*e.g.*, ref. 2). Another approach to fashion a system that is more readily p-doped is to consider systems with mixed Cu/Ag.

1 Z.-K. Yuan, S. Chen, H. Xiang, X.-G. Gong, A. Walsh, J.-S. Park, I. Repins and S.-H. Wei, *Adv. Funct. Mater.*, 2015, **25**, 6733–6743, DOI: **10.1002/adfm.201502272**.

2 C. Ma, H. Guo, K. Zhang, N. Yuan and J. Ding, *Mater. Lett.*, 2017, **186**, 390–393, DOI: **10.1016/j.matlet.2016.10.013**.

Jonathan J. S. Scragg asked: The point was made that chalcogenides tend to suffer from a V_{oc} deficit. Looking more at the sub-groups, one could make a case that the sulfides tend to have worse deficit than the selenides, and possibly that the tellurides are performing best. How deep does this issue go – can you speculate? Does the V_{oc} deficit of sulfides arise from some feature of sulfur itself that impacts electronic properties? Or is it rather to do with a synthesis chemistry that disadvantages sulfides over selenides (and chalcogenides over *e.g.* halides)? Also, could you hold up an example of an "excellent" sulfide material, *e.g.* with high luminescence efficiency, that could demonstrate the opposite?

David Mitzi answered: One pathway that may lead to worse defect properties for sulfides, relative to selenides (and possibly tellurides) simply relates to associated band gaps. For a given structure type, sulfides will tend to have larger band gaps than corresponding selenides and tellurides. As the band gap increases, the defect states associated with crystallographic imperfections will tend to reside deeper within the band gap and therefore be more active with respect to recombination. In terms of "synthesis chemistry", it is possible that the higher volatility of sulfur relative to selenium/tellurium may make it more challenging to avoid certain types of defects (*e.g.*, chalcogen vacancies). In many cases, I believe that these issues can be dealt with by controlling the synthesis pathway (*e.g.*, including a chalcogen vapor during at least some stage of absorber formation). Importantly, moving to heavier chalcogen does not always lead to more defect-friendly materials. CdTe (key commercialized thin-film material) has suffered from V_{oc} deficit for decades. Only recently are CdTe devices being made with reduced V_{oc} deficit (*e.g.*, see ref. 1).

1 J. M. Burst, J. N. Duenow, D. S. Albin, E. Colegrove, M. O. Reese, J. A. Aguiar, C.-S. Jiang, M. K. Patel, M. M. Al-Jassim, D. Kuciauskas, S. Swain, T. Ablekim, K. G. Lynn and W. K. Metzger, *Nat. Energy*, 2016, **1**, 16015, DOI: **10.1038/nenergy.2016.15**.

Jonathan Major remarked: This is a follow up on Jonathan J. S. Scragg's question and what David Mitzi was saying. I think what you have got to think about is the idea of polycrystallinity and the V_{oc} losses involved in that. The reason I say that is from the cadmium telluride world, where I think it was mentioned, possibly in David's talk, about single crystal devices that get a V_{oc} of about 1.1 V, which is a significantly reduced V_{oc} deficit compared to the polycrystalline version. So those losses seem to be more inherent in the structure of the films and the polycrystallinity, than in the chalcogenide nature of the materials themselves.

Sreekanth Mandati enquired: Is it the ionic bond nature in perovskites that makes them unique materials to attain maximum V_{oc}? Perovskites formation appears to be a straightforward ionic reaction between MAI and PbI_2. While, is the covalent nature of bonding in CIGS, CZTS and similar materials in any way responsible for their low V_{oc}? Your views are appreciated.

David Mitzi responded: Lead-iodide-based perovskites indeed offer significant ionic character and this coupled with the electronic configuration of the Pb and I atoms appears to play a role in generating the rather unique band structure and defect characteristics of this system (see, for example, ref. 1). I find it difficult to *a priori* predict how "defect resistant" a particular semiconductor (collection of atoms in a particular crystal structure) will end up being. The defect resistance evidently arises from the nature of states contributing to the band edges, as well as the screening potential of the material (*e.g.*, dielectric constant). Interestingly, I think that there has been a recent prediction that GeSe may be "defect tolerant," due to an antibonding valence band maximum derived from Ge 4s–Se 4p coupling,[2] similar to the case for halide perovskites. However, current champion devices based on this material still show low V_{oc}.

1 W.-J. Yin, T. Shi and Y. Yan, *Appl. Phys. Lett.*, 2014, **104**, 063903, DOI: 10.1063/1.4864778.
2 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, DOI: 10.1038/s41467-021-20955-5.

Susanne Siebentritt remarked: Jonathan J. S. Scragg asked if there are reasons why generally the sulfides are more difficult for solar cells than the selenides.

I think, it is at least partly due to the wide bandgap. In general, defects tend to remain at the same absolute energy, *i.e.* they get deeper when the bands move away from them. For the example where the Ga-on-Cu antisite in $CuGaSe_2$ becomes shallow in low band gap $Cu(InGa)Se_2$, see ref. 1 for the theory, and ref. 2 for experiments. In fact when we look at deep defect luminescence in $Cu(InGa)(SSe)_2$, we see the same deep luminescence in all of them as soon as the bandgap becomes wide enough.[3] More deep defects means very likely more non-radiative recombination and lower V_{oc}.

1 J. Pohl and K. Albe, *Phys. Rev. B*, 2013, **87**, 245203, DOI: 10.1103/PhysRevB.87.245203.
2 C. Spindler, F. Babbe, M. H. Wolter, F. Ehré, K. Santhosh, P. Hilgert, F. Werner and S. Siebentritt, *Phys. Rev. Mater.*, 2019, **3**, 090302, DOI: 10.1103/PhysRevMaterials.3.090302.
3 S. Siebentritt, A. Lomuscio, D. Adeleye, M. Sood and A. Dwivedi, *Phys. Status Solidi RRL*, 2022, **16**, 2200126, DOI: 10.1002/pssr.202200126.

Jonathan J. S. Scragg said: Further to the question of why don't we have so many high performance sulfide materials and concerning the deep defect in CIGS that seems to stay at the same level regardless of the alloying of In/Ga and S/Se. I understand that this defect accounts for the poorer performance of sulfide CIGS, but in other structures and chemistries we should not necessarily expect the same behaviour. Or should we? Is there some reason that sulfide materials should tend to have deeper defects compared to selenides, for example? Or is it simply that the wider the band gap you have, the more "room" there is for deep defects on the energy scale?

Susanne Siebentritt responded: Exactly: in wider band gap semiconductors, there are always more deep defects. Defects tend to stay at the same absolute energy (has been shown nicely for H related defects by van de Walle and Neugebauer[1]). For chalcopyrites, see Fig. 5 in ref. 2 (our recent review on sulfide materials). Since sulfides tend to have larger band gaps they tend to have more deep defects.

1 C. G. Van de Walle and J. Neugebauer, Universal alignment of hydrogen levels in semiconductors, insulators and solutions, *Nature*, 2003, **423**, 626.
2 S. Siebentritt, A. Lomuscio, D. Adeleye, M. Sood and A. Dwivedi, *Phys. Status Solidi RRL*, 2022, **16**, 2200126, DOI: 10.1002/pssr.202200126.

Byungha Shin remarked: Susanne Siebentritt explained that defect levels remain at a similar position within the gap as bandgap increases, which means defects become deeper and more detrimental. If what Susanne says is right, lower bandgap materials then always have to be advantageous over larger bandgap materials. I am wondering if there is literature surveying V_{oc} loss *vs.* bandgap.

David Mitzi commented: The question of why emerging chalcogenide semiconductors all seem to share a large V_{oc} deficit (compared to the fundamental limit for a given bandgap) is key for those working in this area. It is probably useful to note that lead-halide-based perovskites are relatively unique in terms of their "defect tolerance" and ability to achieve very high V_{oc} within a polycrystalline absorber (*i.e.*, chalcogenides are not alone in terms of the difficulty in overcoming the influence of defects). Notably "defect tolerance" does not mean lack of defects but rather points to the fact that the defects present within the film are not very active with regards to recombination. In GaAs, although an exceptionally high V_{oc} can be achieved (close to the fundamental limit), in this case the high performance is accessible in very carefully grown high-quality single-crystal-like absorbers. Since ideally, we would like to employ polycrystalline films and not have to grow films with a vanishingly small defect density (probably expensive), the question is whether we can induce a similar level of defect tolerance into a metal chalcogenide system as for the lead-halide-based perovskites. Ultimately, doing this will require understanding the bonding characteristics within the chalcogenides, as detailed for the broader family of thin-film absorbers in several reviews on the topic of defect tolerance (*e.g.*, see ref. 1–3). In principle, I am not aware of a reason why a defect tolerant band structure shouldn't be achievable in emerging chalcogenide systems, and there has even been some indication that GeSe may offer opportunity in this regard.[4]

1 R. E. Brandt *et al.*, *Chem. Mater.*, 2017, **29**, 4667–4674, DOI: **10.1021/acs.chemmater.6b05496**.
2 A. Walsh and A. Zunger, *Nat. Mater.*, 2017, **16**, 964–967, DOI: **10.1038/nmat4973**.
3 A. Zakutayev, C. M. Caskey, A. N. Fioretti, D. S. Ginley, J. Vidal, V. Stevanovic, E. Tea and S. Lany, *J. Phys. Chem. Lett.*, 2014, **5**, 1117–1125, DOI: **10.1021/jz5001787**.
4 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, DOI: **10.1038/s41467-021-20955-5**.

Conflicts of interest

There are no conflicts to declare.