












Bulk and surface characterisation techniques of solar absorbers: general discussion

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DOI: 10.1039/d2fd90056d

Sreekanth Mandati opened a general discussion of one of the papers by Susanne Siebentritt: If the full width at half maximum (FWHM) of the PL peak is larger, is the quasi Fermi level splitting (qFLs) accurate (<https://doi.org/10.1039/d2fd00057a>)? What if we have shoulder peaks?

Susanne Siebentritt replied: If the FWHM of the PL peak at room temperature is 100 meV or larger, the qFLs is underestimated by 20 mV or more. But if you can measure external radiative efficiency (ERE) or photoluminescence quantum yield (PLQY), you still get a reliable measurement of the non-radiative loss.

Sreekanth Mandati asked: What will be the impact of an extra shoulder to the PL peak on the estimation of qFLs?

Susanne Siebentritt answered: If the shoulder is on the low energy side, it would not change anything.

If the shoulder is on the high energy side (and small) I would make sure that the fit region is far enough away from the shoulder. But if it is significant, I would say, it's first important to get an idea what causes the shoulder.

One thing that can distort the PL spectrum is interference. There is an easy way to check that: keep the PL setup as is and change the angle under which the PL light is detected (ideally between along the normal and nearly grating). The maxima and minima in the spectrum will shift.¹

1 M. H. Wolter, B. Bissig, P. Reinhard, S. Buecheler, P. Jackson and S. Siebentritt, Correcting for interference effects in the photoluminescence of Cu(In,Ga)Se₂ thin films, *Phys. Status Solidi C*, 2017, **14**, 1600189.

Aron Walsh said: Many emerging photovoltaic absorbers have unconventional crystal structures and in turn unusual electronic structures. There may be highly non-parabolic band dispersion, multiple valleys in reciprocal space, or indirect bandgaps. Is your method and PL analysis still applicable in such cases?

Susanne Siebentritt answered: The PL and absorbance analysis makes no assumptions about the electronic structure. In fact most of the absorption onset has nothing to do with nice electronic structures as calculated for ideal crystals. There is disorder and tails and bandgap fluctuations.

It doesn't matter: as long as there are states that are available for optical transitions, we see them in absorption and in luminescence and the theory of detailed balance works. It does not depend on the details of electronic structure and E - k dispersion maxima.

Charles J. Hages queried: These measurements are clearly sensitive to the temperature. When you refer to the 'measurement temperature' what is this referring to? Is this the room temperature or the actual temperature measured (*e.g. via* pyrometer) on the sample under illumination?

Susanne Siebentritt replied: What is important is the actual sample temperature under laser illumination.

We measure it by measuring the actual temperature of the lab and by observing the sample through a thermal camera. With this we see if the laser spot heats up – but this happens typically only at fluxes much higher than 1 sun.

Thomas P. Weiss said: We talked about PL on semiconductors with different valence bands located at different energies. Under which circumstances will these different valence bands show up at separate band-to-band peaks in a PL spectrum?

How can these different peaks, possibly arising due to several valence bands, be distinguished from defect related PL peaks? Are there complementary methods to check for the assignment of the PL peaks? Would the measurement of the absorption coefficient be sufficient? As long as the bandgap with the smallest energy (highest lying valence band) has a sufficient large absorption coefficient, it should be fine?

Susanne Siebentritt responded: At low temperatures (~ 10 K) it is much easier to distinguish between excitons and defects. In fact, the different bandgaps in chalcopyrites lead to the corresponding excitonic emissions at low temperature PL. At room temperature the different bandgaps are not very likely to appear in PL, because the carriers thermalise to the lowest band (in deed, thermalisation is less effective a low temperatures, because the optical phonons do not exist). If there are several peaks at room temperature, I would always cool down and see how they evolve at low temperatures – and then measure excitation dependence, to distinguish between excitonic and defect bands. Of course if there are

significant fluctuations, also at low temperature the PL emission will be broad. Still, from the temperature and excitation intensity dependence, one can generally extract what is defect related and what is band(tail)–band(tail).

Mirjana Dimitrievska added: Are defects really one of the biggest factors to influence the V_{oc} deficit? In our case, we have nice monocrystalline absorbers which do not give any working solar cells, and then polycrystalline samples that have very nice efficiencies (<https://doi.org/10.1039/d2fd00055e>). What is the limitation to the solar cell performance in that case?

Susanne Siebentritt answered: A nice paper to start the discussion:¹

Briefly: you need an asymmetry, either a p–n junction or selective contacts.

Your contacts on the single crystals are never the same as in polycrystalline (because you grow the polycrystalline film on one of the contacts, *i.e.* you anneal this contact – usually for a long time). If the solar cell is based on a p–n junction, you need sufficient doping.

And it is possible that the polycrystalline films do have fewer deep defects, because the defects diffuse towards the grain boundaries and anneal there. The PL you showed on the single crystals does show a large deep defect. And the measurements stop at 1.2 eV, so there could be more deeper defects.

V_{OC} deficit depends on non-radiative recombination. This can happen at interfaces and at defects – so yes deep defects are a big problem for V_{OC} . If it's the biggest problem or not, depends on the interfaces.

1 T. Kirchartz and U. Rau, *Adv. Energy Mater.*, 2018, **8**, 1703385.

Jonathan J. S. Scragg asked: You stated that the interfaces obtained in devices made from epitaxial thin films (of CIGS) are not as clean as you'd like them to be – could you elaborate on that statement? What do you mean and why are the interfaces not clean?

Susanne Siebentritt responded: First of all we can have unfavourable band alignment. I think that's the case between CIGSe and GaAs.

Then there is never an ideal lattice match, which causes dislocations and/or strain at the interface.

In general, epitaxial films show many more dislocations than polycrystalline films. See *e.g.* ref. 1. In polycrystalline films any lattice imperfections can diffuse to the grain boundaries, which are no more than 1 micrometer away and annihilate there. In epitaxial films they have nowhere to go.

Also, very often we find Kirkendall voids at the interface¹ – that can't be good for the V_{oc} . Another reason for lower electronic quality in epitaxial films is probably the lack of alkalis.

Good epitaxial CIGSe solar cells are made with alkali treatments.²

1 C. H. Lei, A. A. Rockett and I. M. Robertson, *J. Appl. Phys.*, 2006, **100**, 114915.

2 J. Nishinaga, T. Nagai, T. Sugaya, H. Shibata and S. Niki, *Appl. Phys. Express*, 2018, **11**, 082302.

Byungha Shin asked: In the original SQ theory, non-radiative V_{oc} loss is $kT \ln(\text{EL}_{\text{EQE}})$, where EL_{EQE} is electroluminescence quantum efficiency, while in

eqn (5) in your manuscript you used PLQY. Would the use of PLQY in place of EL_{EQE} cause any error in estimating V_{oc} loss?

Susanne Siebentritt replied: With PLQY we can determine qFIs loss – this is identical to the V_{OC} loss only if transport does not play a (major) role for the EL spectrum (in that case the PL spectrum and the EL spectrum (at V_{OC}) would be identical) and if the interfaces don't add more V_{OC} loss.

Nicole Fleck opened a general discussion of the paper by Marcus Bär: Most of the HAXPES peak fitting in your article (<https://doi.org/10.1039/d2fd00056c>) is done with a Shirley background, however the Sb 3/2 is fitted with a linear background. Could you comment on or explain this methodology choice?

Marcus Bär replied: There is no physical reason for the choice of the different backgrounds used in the fits of the different core levels in this particular article and thus there is also no hidden methodology meaning. As a matter of fact, close inspection of the fits will show you that the spectra that have been fitted using Shirley backgrounds could have easily been also fitted using linear backgrounds (with no impact on the fit quality) as well.

Mohit Sood asked: You use an indirect method to estimate the possible conduction band offset (CBO) at the absorber/buffer interface. Given the fact that there is significant intermixing at the interface, how accurate would you say this approach is?

Marcus Bär answered: Indeed, the reason for the largest uncertainty in the energy level alignment scheme in Fig. 8 in our article (<https://doi.org/10.1039/d2fd00056c>) is the lack of a direct measurement of the CBMs of the absorber and buffer by, *e.g.* inverse photoemission. Instead we used the buffer and absorber bulk bandgap energies together with the relation $CBO = E_g^{buffer} - E_g^{absorber} + VBO$ to basically estimate the CBO. Any deviation from the underlying assumption that the bulk bandgaps also represent the (opto) electronic structure close to the (interdiffused) buffer/absorber interface will have a direct impact on the estimated CBO. In our considered case of the composition of a Cu-deficient absorber and the potential incorporation of Cd and Zn in the topmost absorber region, we assume that the 'true' absorber bandgap (close to the interface) will be enlarged, pushing the absorber CBM away from the Fermi level (E_F). Thus, we consider the derived 'cliff'-like CBO at the CuSbS₂/(Cd,Zn)S:Ga interface of -0.35 eV to be rather a lower boundary for the real CBO than a value that we can assign an experimental uncertainty to.

Mohit Sood asked: "For CuSbS₂ we find a surface composition that is Cu-poor compared to the expected [Cu : Sb] : [S] 1 : 1 : 2 composition (see discussion above). For Cu-chalcopyrites this usually leads to a reduction of the p–d repulsion of the Cu and S derived states that dominate the VB, resulting in a VBM shift away from E_F ." Your measurements suggest that the E_F is rather close to the VBM in CuSbS₂. Does that mean in this case the Cu deficient surface leads to a higher CBM?

Marcus Bär answered: In the context of the concept that the p–d repulsion of (in this case) S and Cu derived states determine the VBM position, our finding of a Cu-deficient CuSbS₂ surface composition and an absorber VBM position close to E_F indeed seems contradicting. There could be many explanations for this experimental finding, of which I list the most likely ones below:

(1) The CuSbS₂ VBM position close to E_F was derived by a very surface sensitive method, *i.e.* any surface contaminants or effects due to the absorber cleaning, *e.g.* by KOH, may induce an (upward) band bending at the absorber surface, resulting in a VBM close to E_F .

(2) The CuSbS₂ might be a higher p-type doped than, *e.g.* Cu-chalcopyrites and/or it might not exhibit the pronounced (downward) surface bending that is observed for CIGSe, resulting in a VBM close to E_F (especially compared to the electronic surface structure of Cu-chalcopyrites).

(3) The electronic structure of CuSbS₂ is (mainly due to the presence of Sb p-derived states) significantly different to that of, *e.g.* Cu-chalcopyrites, so that the p–d repulsion effect related to S and Cu related states is not as pronounced, and/or for stoichiometric (or Cu-rich) CuSbS₂ the VB states are expected to be cut-off by the Fermi edge. As a matter of fact in early CuSbS₂ work,¹ one does find spectral intensity around the Fermi edge in UPS measurements.

However, (and somewhat independent of the above discussion) there are also reports in the literature² that not only link the degree of absorber Cu-deficiency to a (decreased) p–d repulsion induced VBM shift away from E_F , but that also report on a CBM shift away from E_F at the same time. This is also the reason why we tried to visualize this effect in Fig. 8 (<https://doi.org/10.1039/d2fd00056e>) in our article by shading the area.

1 B. Yang, L. Wang, J. Han, Y. Zhou, H. Song, S. Chen, J. Zhong, L. Lv, D. Niu and J. Tang, *Chem. Mater.*, 2014, **26**, 3135.

2 M. Bär, J. Klaer, L. Weinhardt, R. G. Wilks, S. Krause, M. Blum, W. Yang, C. Heske and H.-W. Schock, *Adv. Energy Mater.*, 2013, **3**(6), 777.

Charlotte Platzer Björkman asked: There was a lot of Ga at the interface – what compound do you think you have there?

Marcus Bär answered: Indeed, the Ga/(Ga + Zn + Cd) ratio approaches 30% at the buffer/absorber interface. This enhancement is accompanied with an increase of the Cu content in the interface region of the buffer (which is, however, on a much lower level – see Fig. 6 in our article). Given that there is sufficient S present on both sides of the interface, one could speculate that a Ga–S-type interfacial species is formed, but our data does not provide any proof for that hypothesis.

Cara Hawkins said: There is a 2nd contribution (highlighted in green, Fig. 4 and 5 in your article) in your HAXPES data for Cd 3d_{5/2} and Zn 2p_{3/2}, which you tentatively ascribe to different chemical environments limited to the buffer–absorber interface; how could you characterise the origin of this contribution more specifically?

Marcus Bär responded: One way to gain more insight on the chemical structure of this ‘interface layer’ would be to consult the Zn LMM and Cd MNN XAES

spectra and see whether they also indicate the presence of two species (unfortunately, we have not measured this data for this sample set). If there is an indication that also the Auger spectra indicate the presence of two species, then one could try to extract the Auger spectra of the different chemical (Zn and Cd) species, allowing (together with the information from the core levels) to compute the modified Auger parameters, which are very powerful to identify different chemical environments.

In addition, one could try to prepare a nice cross section lamella to be studied by TEM (and EELS) to gain additional insight on the chemical interface structure.

Mirjana Dimitrievska queried: Considering that CdS creates so many problems for the absorber, is there any other alternative material that would be better suited as a buffer layer?

Marcus Bär replied: This work is in fact on (Cd,Zn)S:Ga buffer layers, which are thought to belong to the “low electron affinity” (or high conduction band minimum) buffer materials, as Prof. Mitzi referred to in his plenary lecture. However, it seems that based on our measurements the buffer layer (with a derived Zn/(Zn + Cd) ratio of approximately 0.2) is still ‘CdS-like’ and thus the Zn content should be further increased in order to improve the energy level alignment to the CuSbS₂ absorber. However, as we have already observed sample charging in our measurements, increasing the Zn content further could decrease the electrical conductivity in the buffer to a point where it might negatively affect the solar cell’s series resistance. Prominent alternative buffer materials are (Zn,Mg)O, Zn(O,S), (Zn,Sn)O...

Mirjana Dimitrievska asked Marcus Bär: Have you tried alternative buffer layers? TiO₂ worked really well for us, would this be a good option for you too?

Marcus Bär responded: No, to my knowledge our collaborators from NREL (that are experts in device manufacturing/optimization) have not tried TiO₂ as alternative buffer layer. Based on the fact that for TiO₂ the distance between CBM and Fermi level is presumably smaller than compared to what we find for the (Cd,Zn)S:Ga buffer, I would not expect an improvement with respect to the negative CBO situation.

Matias Valdes asked: A question related to the SbO_x contribution seen on the spectrum, probably located on the surface and not removed by etching: the signal increases as the buffer layer thickness becomes higher – could it be buffer layer deposition promoting partial oxidation of the CuSbS₂ film?

Marcus Bär responded: Indeed, the contribution of the Sb 3d attributed to SbO_x is increasing relative to the contribution attributed to CuSbS₂ with increasing (Cd,Zn)S:Ga thickness. This let us conclude that the oxide species is located close to the absorber surface. In that respect, yes, the partial oxidation uncovered CuSbS₂ during the buffer atomic layer deposition (ALD) process might be a likely explanation.

Matias Valdes remarked: Have you tried to change etching time to see if any Sb oxide contribution can be removed?

Marcus Bär responded: Our standard procedure was to etch the as-received CuSbS₂ 30 min in 0.1 mol L⁻¹ aqueous KOH solution as this was also the standard etch treatment for device preparation prior to buffer deposition. Thus, we did not do any systematic etch study, but we tried extended etching times of a few hours once or twice, that led to no significant difference to the result that we got after 30 min etching.

Susanne Siebentritt commented: It seems every Cu-containing semiconductor is Cu-poor at the surface.

Cu is very mobile – could that be an artefact of the measurement?

Did anybody ever measure a stoichiometric surface in a Cu-containing semiconductor?

Marcus Bär answered: Yes, Cu is very mobile (particularly in Cu-deficient areas of Cu-chalcopyrites) and there have been reports about the effects of externally applied¹ or internally present² electric fields on the chemical and electronic structure profiles. Thus, a downward surface band bending (as often observed for Cu-chalcopyrites) would indeed be a driving force to push the Cu⁺ ions into the absorber bulk, resulting in a Cu-deficient surface. However, it is not clear whether this electric field at the absorber surface would be sufficient to cause this electromigration. In addition, starting from the pioneering work by Schmid *et al.*^{3,4} to recent XPS studies⁵⁻⁷ there are many records in the literature that report stoichiometric Cu/(In + Ga) surface compositions for Cu-chalcopyrites. However, the latter seems to be very sensitive to the absorber bulk composition, resulting in significant Cu-deficient surfaces for Cu-poor or even stoichiometrically grown Cu-chalcopyrites, while Cu-rich grown absorbers result in the formation of Cu_{2-x}Se surface phases. The fact that the absorber bulk composition regime (being slightly Cu-rich) that results in a stoichiometric Cu/(In + Ga) surface composition seems to be very narrow, together with the fact that most XPS studies focus on solar cell relevant Cu-chalcopyrites (*i.e.*, study Cu-deficient absorbers that result in the highest efficiencies), are the likely reasons for the XPS-derived Cu-poor surface compositions reported in the majority of related literature. In conclusion, there is no indication that the Cu-poor surface found by XPS for many Cu-chalcopyrites is a measurement artefact; it is rather a result of a complex interplay between the bulk and surface structure.

1 G. Dagan, T. F. Ciszek and D. Cahen, *J. Phys. Chem.*, 1992, **96**(26), 11009.

2 I. Lubomirsky, K. Gartsman and D. Cahen, *J. Appl. Phys.*, 1998, **83**, 4678.

3 D. Schmid, M. Ruckh, F. Grunwald and H. W. Schock, *J. Appl. Phys.*, 1993, **73**, 2902.

4 D. Schmid, M. Ruckh and H. W. Schock, *Appl. Surf. Sci.*, 1996, **103**(4), 409.

5 A. Hofmann and C. Pettenkofer, *Surf. Sci.*, 2012, **606**, 1180.

6 H. Mönig, Ch.-H. Fischer, R. Caballero, C. A. Kaufmann, N. Allsop, M. Gorgoi, R. Klenk, H.-W. Schock, S. Lehmann, M. C. Lux-Steiner and I. Lauermaun, *Acta Material.*, 2009, **57**(12), 3645.

7 R. Félix, A. Weber, O. Zander, H. Rodriguez-Álvarez, B.-A. Schubert, J. Klaer, R. G. Wilks, H.-W. Schock, R. Mainz and M. Bär, *J. Mater. Chem. A*, 2019, **7**, 2087.

Susanne Siebentritt said: You have significant interdiffusion. How should I think about the band alignments, that you show:

Is it that the band alignment at the interface and the gradients come on either side of it?

Or is it that the band alignment between the bulk and the gradients come between the two band diagrams?

Marcus Bär replied: The scheme shown in Fig. 8 of the manuscript depicts the electronic structure directly at the interface. The approach that was chosen to determine the VBO actually includes any effect caused by interdiffusion (and interface induced band bending) as it was basically derived from one VB spectrum that directly shows how the VBMs of the buffer and absorber align when brought into contact.

However, we see two main (interdiffusion related) uncertainties with respect to the depicted energy level alignment:

(1) The Cu that diffuses into the (Cd,Zn)S:Ga buffer will in a first approximation lead to the formation of Cu-derived states close to the VBM, resulting (depending on their concentration) in a related defect level above the VBM within the buffer bandgap or in a Cu-derived VBM located much closer to E_F . The rather large foot (*i.e.*, the significant deviation of the difference spectra from the linear extrapolation of the leading edge in the VBM region in Fig. 6) might be an indication for the presence of these Cu-derived VB states. In the latter case (the Cu-derived states form the VBM) the ‘true’ buffer VBM will move towards E_F (as indicated by the shadowed area in Fig. 8) resulting in VBO reduction.

(2) The biggest source of uncertainty is certainly the lack of a direct measurement of the CBM positions for the buffer and absorber by, *e.g.* inverse photoemission. So we use $CBO = E_g^{\text{buffer}} - E_g^{\text{absorber}} + VBO$ to basically estimate the CBO. This method assumes that the bulk bandgaps also represent the (opto) electronic structure close to the buffer/absorber interface. For CuSbS₂, we find a surface composition that is Cu-poor compared to the expected [Cu] : [Sb] : [S] = 1 : 1 : 2 composition (see discussion in our manuscript). For Cu-chalcopyrites this usually leads to a reduction of the p–d repulsion of the Cu and S-derived states that dominate the VB,¹ resulting in a VBM shift away from EF. For CuInS₂ also a shift of the CBM away from EF could be observed experimentally.² The incorporation of Zn and Cd in the upper region of the absorber is expected to result in a larger bandgap as well. While the change in the VBM position of the absorber is considered by the VBO determination approach here, the impact of the Cu-deficiency (that might even increase upon interface formation and Cu out diffusion into the buffer) and of the potential incorporation of Zn and Cd in the topmost region of the absorber on the CBM position is not included in the approach of CBO estimation based on the buffer and absorber bulk bandgap difference. However, both (the absorber Cu-deficiency and the Cd and Zn incorporation) are assumed to push the absorber CBM away from E_F (as indicated by the shadowed area in Fig. 8), resulting in an increase of the derived ‘cliff’-like CBO.

1 S.-H. Wei and A. Zunger, *J. Appl. Phys.*, 1995, **78**, 3846.

2 M. Bär, J. Klaer, L. Weinhardt, R. G. Wilks, S. Krause, M. Blum, W. Yang, C. Heske and H.-W. Schock, *Adv. Energy Mater.*, 2013, **3**(6), 777.

Joachim Breternitz remarked: Thinking from a chemical point of view – and this might be voluntarily simplistic – one could think that buffer and absorber are very similar in that they are both sulfides, which may facilitate the Cu-diffusion along the concentration gradient. Do you believe it would be a valuable approach to consider chemically different buffer/absorber combinations to prevent diffusion between the layers?

Marcus Bär answered: Yes, this might be good suggestion... if diffusion is deteriorating the cell performance. In some occasions, however, it seems that you actually do want to have some chemical interaction at the interface.

Rachel Woods-Robinson opened a general discussion of the paper by Mirjana Dimitrievska: Previous calculations of ordered zinc blende Zn_3P_2 , have predicted a light hole band just a few tens of meV below the VBM.^{1,2} Additionally, the transition from VBM-to-CBM have been reported as optically forbidden under some conditions, depending on the polarization of light.³ Dr Dimitrievska and colleagues have observed an additional PL peak in their Zn_3P_2 thin films (<https://doi.org/10.1039/d2fd00055e>); I am not an expert in PL, but is it possible this additional observed peak could be due to the combined effect of allowed transitions from the light hole band and optically forbidden transitions at the VBM-to-CBM?

1 D. M. Stepanchikov and G. P. Chuiko, *Condens. Matter Phys.*, 2009, **12**(2), 239.

2 Data retrieved from the Materials Project for Zn_3P_2 (mp-2071) from database version v2021.11.10.

3 J. Misiewicz, *J. Phys.: Condens. Matter*, 1990, **2**(8), 2053.

Susanne Siebentritt clarified: I'm not exactly sure, what you mean by the additional peak.

The peak at lower energies is most likely a defect peak.

The situation you describe is actually similar to that of chalcopyrites. The fundamental bandgap transitions are only allowed for polarised light (either parallel or perpendicular to the *c*-axis) in absorption as well as in luminescence. The VBM is split into three separate bands. In some compounds, *e.g.* CuInS_2 or CuInSe_2 the split is also very small, a few meV. One cannot expect to see this split in room temperature PL, because the peak is too broad to resolve it. If the split is larger, it's also unlikely to see it in room temperature PL, because carriers are thermalised and the lower VB will not be occupied.

If the crystals are good and we see excitons, we can see the excitons of all three VBs in PL at 10 K or below. But the PL peaks presented are too broad to be nice excitons.

Mirjana Dimitrievska replied: Thank you for the interesting question. Yes, indeed, in general some peaks in PL could be related to forbidden transitions. However, in our case we tend to believe that this peak is indeed related to defects, as its temperature and laser power behaviour seem typical of defect related transitions. This detailed investigation and the assignment on the origin of the peak have been reported in ref. 1.

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

Thomas P. Weiss continued the discussion of the paper by Marcus Bär: In light of the various effects happening at the heavily intermixed (Cd,Zn)S:Ga/CuSbS₂ interface (<https://doi.org/10.1039/d2fd00056c>):

Do you know if the quality of the absorber (including front surface recombination), improves upon the deposition of the buffer layer?

For instance, did you measure the photoluminescence before and after the buffer layer deposition?

Marcus Bär replied: No, this is information we do not have/a measurement that has not been performed. However, combining PL measurements with our X-ray spectroscopic analysis has been long on the list of things that we would like to implement in the future.

Susanne Siebentritt added to all: We prefer sharp interfaces, because we describe them analytically. Did anybody compare graded *vs.* sharp interfaces in a simulation?

David J. Fermin remarked: Can we consider the junction in organo halide perovskite devices as 'sharp'? That would be an example of a high-performance device based on sharp boundaries.

David J. Fermin asked: Could you envisage the case that compositional grading and intermixing could lead to a situation in which charge separation can be promoted within the 'absorber layer' rather than at the absorber/buffer interface?

Marcus Bär replied: Yes. One could consider 'traditional' CdS/CdTe-based devices (where the 'activation treatment' causes significant intermixing) or even the compositional grading in CIGSe absorbers as examples, I think.

Rafael Jaramillo added: In cases when the p-n junction becomes diffuse (*e.g.* due to intermixing between absorber and contact layers), the cliff/spike conduction band offset becomes somewhat less important, as the location of peak recombination activity moves away from the metallurgical junction. Maybe a small effect, but it could be modelled.

Rachel Woods-Robinson commented: We have been discussing the application of measurements such as HAXPES to investigate new "unusual" materials. I am not an expert in this measurement technique so please correct me if this understanding is too basic, but to my understanding HAXPES is an optical method which is used for example by Hartmann *et al.* to estimate electronic properties. Usually this works well for probing materials with direct allowed VBM-to-CBM transitions as is the case for the CuSbS₂ you report. However, if there was a forbidden optical transition at the VBM-to-CBM (as has been reported for Zn₃P₂,¹ among many other materials), could this state be probed with HAXPES? If not, could this lead to incorrectly identified electronic properties?

1 J. Misiewicz, *J. Phys.: Condens. Matter*, 1990, 2(8), 2053.

Marcus Bär responded: No, HAXPES is not an optical method. It is based on the external photoeffect, *i.e.* photo-excited electrons leaving the sample are probed and their kinetic energy is measured. Thus (HAX)PES probes the total density of occupied states, and once the photoelectrons have enough energy to leave the sample, there are no 'forbidden' transitions. Thus the energy levels closest to the Fermi level are responsible for the VBM derived by (HAX)PES. This is the VBM that describes the true electronic structure. However, if for whatever reason, optical transitions from that energy level to the CBM are not allowed, then the optical bandgap deviates from the electronic bandgap.

Vaidehi Lalpalikar asked all: Considering that the VBM of Cu(Sb/Bi)₂S₂ is made of Cu-3d states and Cu is in the +1 oxidation state, do you expect these materials to hold up their performance in a solar cell under continuous operation? Photo-excitation would oxidize Cu +1 to +2 which would eventually compel the absorber material to undergo some chemical transformation to balance the charges. Although it is the case with CIGS as well, Cu in Cu(Sb/Bi)₂S₂ seems more prone (experimentally) to such oxidation.

Thank you!

Devendra Tiwari opened the discussion of the paper by Rafael Jaramillo: Thanks for insightful results. The PL data on Ba₂ZrS₃ from Professor Jaramillo's group shows that the PL of a single crystal and epitaxial films show poor PL yield (<https://doi.org/10.1039/d2fd00047d>). I suggest that could be due to the exceptionally low thermal conductivity of Ba₂ZrS₃. This would mean a high photon fluence of energy > E_g during PL measurements. From my memory an excitation of 10¹⁹⁻²⁰ of Ar lines of 457 or 514.5 nm, on a very small area was quoted in response to a comment from Professor Siebentritt, under which one would deposit a lot of localised heat. This may either lead to local compositional or structural changes. As indicated by Professor Jaramillo, no such compositional changes were detected. Yet, at they very least, the samples would have had a high local temperature which will lead to considerable broadening and lowering of the intensity of the PL peak as is widely seen in experiments, as the PL intensity decays inversely with temperature (1/T¹⁻²). Further, the presence of any extended defects such as twin boundaries, as indicated by the presenter, would confine the phonon modes further and make the dissipation of heat even worse. Thus fundamentally, it again points to the same reasoning. As a check for future work, you could perform the measurements in an immersion cryostat which provides better heat dissipation. A typically used 0.2–0.5 W @ 5 K capacity optical cryostat with a sample mounted in conductive contact with a cold finger would not provide a good heat sink in such a case.

Rafael Jaramillo replied: Thank you for the note. Yes the thermal conductivity is exceptionally low, we have a project on this that unfortunately isn't published (yet). I hadn't considered that this could lead to such an effect in PL measurements, but we will pursue this analysis, I am very appreciative!!

Mirjana Dimitrievska asked: Regarding your observation that the PL spectra looks very different when measured on different forms of materials (powder, epitaxial film and thin film). Could you please provide some more insight into why this is the case? Maybe your own idea into what might be happening?

Rafael Jaramillo responded: Hi Mirjana, thanks for the discussion at the meeting. I suspect that the powders are comprised of mostly small single crystals, and it seems that their surfaces are naturally passivated. The crystals could have two things going against them: one, they could have a high twin boundary density, and two, they are self-absorptive. My hypothesis for the thin films is that the PL is affected by quenched crystal disorder in the form of extended defects, mainly those twins that are so interesting. But that's just a hunch, we haven't proven anything. There is of course always the possibility of unknown, lifetime killing extrinsic defects, that can take a while to sort out. For instance, the crystals are grown in a BaCl_2 flux – who knows about the effects of Cl point defects!

Phillip J. Dale commented: You mentioned that when comparing powder samples, thin films, and single crystals, that the PL yield was significantly bigger for the powder samples. I imagine they were all grown in different chemical environments, so they may contain different impurities, have you been able to investigate this?

Rafael Jaramillo replied: Yes of course! This is always a significant wildcard. The powders are made from nominally pure precursors. We haven't done trace analysis.

The crystals are made from nominally pure precursors, plus a BaCl_2 flux. The effect of Cl is a big unknown. We haven't done trace analysis.

The epi films are made from nominally pure precursors plus hydrogen, which comes in the form of H_2S . We don't know the effects of H incorporation. We haven't done trace analysis.

Rokas Kondrotas remarked: Regarding weak PL in BaZrS_3 single crystals/thin-film. We also observed a similar effect on SnZrSe_3 (not a perovskite structure though). Do you have any idea why powder PL is more efficient? Did you try measuring PL at low K for single crystal/epitaxial films? I found that after long storage of SnZrSe_3 in ambient (especially over summer when humidity was high) there was significant increase in oxygen content in the powder samples while the single crystal did not show the same trend. So I was wondering if there is correlation between surface oxidation and PL yield?

Rafael Jaramillo responded: Interesting. We don't suspect oxidation is playing a role, although we should always re-evaluate this. The oxidation of BaZrS_3 seems to trend with crystal quality, and in our higher quality samples we see basically nothing in terms of long-term degradation. Same with water stability, it seems to depend on crystal quality. But humidity is always a problem for semiconductor materials research, and we will continue to consider it.

We don't have any firm idea to explain the PL trend yet, beyond the hypotheses that were discussed at the meeting. I hope we can develop these further and

publish something soon! I'm very interested to hear about the SnZrSe₃ work, can you please send a preprint or something similar? Thank you.

Aron Walsh asked: I was interested in the longer diffusion length that you report for the Ruddlesden–Popper phase. This structure is layered and I expect that the transport properties will differ substantially in the stacking direction. Do you take this into account for your carrier lifetime and diffusion length analysis?

Rafael Jaramillo answered: Hi Aron, our time-resolved photoluminescence (TRPL) measurements on the layered, 327 phase were on samples with the basal plane exposed. Our modeling was 1D. Therefore, our TRPL results are nominally for cross-plane transport, which should be the slow transport direction.

Our IR reflectivity measurements include samples prepared with the basal plane exposed (*c*-axis vertical), and measurements on samples sectioned to place the *c*-axis in-plane. For those measurements, we used polarized IR beams and rotated the samples, to measure the transport anisotropy. The measure of mobility anisotropy between in-plane and out-of-plane transport was much smaller than theoretical predictions (only DFT effective mass). This highlights the need to theoretically model scattering, which of course isn't news to you! IR results are available.¹

1 K. Ye, N. Z. Koocher, S. Filippone, S. Niu, B. Zhao, M. Yeung, S. Bone, A. J. Robinson, P. Vora, A. Schleife, L. Ju, A. Boubnov, J. M. Rondinelli, J. Ravichandran, and R. Jaramillo, *Phys. Rev. B*, 2022, **105**, 195203.

Jens Wenzel Andreasen remarked: Could you please explain how you determined the presence of a twin boundary?

Rafael Jaramillo replied: By analyzing the ZrS₆ octahedral tilt in the STEM data. It's not apparent from the raw data visualized on a low resolution screen (like a projector). But on a high resolution screen it becomes more clear.

Another way to see the boundary is by looking at the corrugation of the Ba atoms. Along one direction, they alternate up/down/up/down. After rotating 90 degrees, the corrugation goes away, and instead the atoms appear blurred, because the corrugation is along the beam direction.

Joachim Breternitz added: We see twin boundaries in halide perovskites as well,¹ but their PL is not weak. Considering your measurements: which crystal faces are you looking at during the measurements, since optical properties are anisotropic in lower symmetry crystal systems?

1 J. Breternitz, M. Tovar and S. Schorr, *Sci. Rep.*, 2020, **10**, 16613.

Rafael Jaramillo answered: Yes, certainly. My suspicion is that the bond angle dependence of the bandgap is weaker in the halides, because they are more ionic. One could calculate using theory or DFT a coefficient describing the dependence of the bandgap on the bond angles along a particular direction (maybe I should do this already...). Then, structure and PL measurements could be connected.

The BaZrS₃ epi films grow with the *b* axis in-plane. This means that there are two, energetically-equivalent orientations, related by a 90 degree rotation of the *b*-

axis around the surface normal. It's a bit painful to describe in a textbox, I hope it's clearly described in our paper.¹

1 I. Sadeghi, K. Ye, M. Xu, Y. Li, J. M. LeBeau and R. Jaramillo, *Adv. Func. Mater.*, 2021, **31**(45), 2105563.

Susanne Siebentritt asked: I very much like the approach to model multiple TRPL decays.

But I have several concerns about the model:

It seems to not be very specific: you can model the decay in BaZrS₃ with a factor 2 different lifetimes and a factor of 15 different mobilities – how sensitive is the model actually to the parameters?

Your spot is tiny. That means you are in high excitation at the beginning of the decay, but you model the decay with low excitation Shockley–Read–Hall (SRH) recombination. And you will have diffusion away from the tiny spot. Is 1-D modeling appropriate?

Rafael Jaramillo responded: Hi Susanne, parameter sensitivity is always interesting. We haven't gone into detail on this yet, but we do ask the software to spit out the confidence intervals, and to visualize the covariance matrix, which just reproduces common sense but it is nice to see.

We don't think the carrier injection is all that high, even at very short times. Maybe just verging on degenerate, *e.g.* low-10¹⁹. Now, with such high dielectric constants, the Mott concentration may be much lower than usual, say in the 10¹⁸ s. So that is a caveat, and maybe the short time electron and hole populations are degenerate. We have varied excitation spot size, and found no significant differences to our estimated μ , τ , and S , within the present statistics. The raw data does evolve, of course. The short-time parameter (Auger) changes in unexpected ways. All this is to tell us that we should move to 2D modeling, yes! Or simply use larger spot sizes always. The trouble with the crystals is that they are very small and often faceted. But the epi films make life easier.

Yevhenii Havryliuk opened a general discussion of the paper by Jens Wenzel Andreasen: What is the thickness limit of the layer that can be recognized by your method (<https://doi.org/10.1039/d2fd00044j>)?

Jens Wenzel Andreasen answered: The resolution, and thus the thickness of a layer that can be uniquely identified from its chemical composition, is determined by the beam size. At 4th generation synchrotrons, hard X-rays may typically be focused to 50 nm.

Jonathan J. S. Scragg said: Several conversations at this meeting have noted the unexpected discrepancies that can be observed between polycrystalline thin films and epitaxial thin films, in terms of optoelectronic properties and device metrics. Is it worth making your correlated measurements of XRF, X-ray beam induced current (XBIC) *etc.* on an epitaxial device, simply as a sanity check, to determine if the epitaxial films do indeed exhibit the expected homogenous properties?

Jens Wenzel Andreassen replied: Certainly, the combination of XBIC and XRF would be ideal for such a verification – even better in combination with scanning 3D X-ray diffraction to unveil strain and crystallographic defects.

Marcus Bär asked: Focused ion and hard X-ray beam sounds destructive. How do you test/account for beam damage?

Jens Wenzel Andreassen replied: I am quite convinced that the focused ion beam technique only alters the surface a little. There may be a little implantation of Ga ions in the top few nm of the surface, but the technique is at the foundation of the well established (destructive) 3D imaging technique combining focused ion beam (FIB) and SEM imaging, and is generally recognized as giving a faithful representation of the structure of the free surfaces generated.

In this context, I believe a more serious problem could be the very generation of these free surfaces, which for the thin ($\sim 1 \mu\text{m}$) lamella will most likely lead to substantial strain relaxation in the constituent layers, which could seriously affect the electronic properties, such that they deviate from the properties of the actual solar cell. Please refer to ref. 1 for details about this effect. Regarding the hard X-ray beam, this is in fact quite gentle, due mainly to the low absorption cross section at high energy. Each point in the map is exposed for only 0.1 second, and we did a degradation test, illuminating the same spot for 15 minutes, where we saw a reduction in X-ray beam induced current of less than 0.5%. At close to three orders of magnitude lower exposure times, we consequently don't expect any degradation effects due to X-ray radiation damage.

1 S. Haratian, F. Niessen, F. B. Grummen, M. J. B. Nancarrow, E. V. Pereloma, M. Villa, T. L. Christiansen, M. A. J. Somers, *Acta. Material.*, 2020, **200**, 674.

David J. Fermin commented: This is a very interesting technique. The XBIC contrast clearly shows areas in which the device structure is compromised (white arrows in Fig. 3 of your article, <https://doi.org/10.1039/d2fd00044j>). However, there are also areas, for example around the $3 \mu\text{m}$ mark, where one can see a clear variation in XBIC, but no major contrast in the XRF images. Can you comment on the possible origin of this contrast?

Jens Wenzel Andreassen answered: A limitation of the 2D implementation reported here is that the XRF images are 2D projections of the chemical and morphological heterogeneities in the $1 \mu\text{m}$ thick lamella. Those variations are thus difficult to distinguish, except in favorable cases where for instance, grain boundaries are fortuitously oriented, close to parallel with the X-ray beam.

At the position indicated, one could speculate if the high level of X-ray beam induced current corresponds to a particularly large CZTS grain, that occupies the full thickness of the lamella.

A 3D implementation of the method is highly advantageous, as it will allow a much better distinction between chemical and morphological variation.

Susanne Siebentritt highlighted: You write in your introduction "silicon solar modules' production is not efficient in terms of energy and material consumption. To become a commercially viable alternative to silicon-based technology,

new generations of solar cells have to be competitive in terms of stability, up-scaling and energy-payback time.” We discussed this for a long time – and could not agree.

I still want to point out, that Si has become incredibly cheap and has an energy pay-back time of less than a year – with 30 years warranty. I don't think this can be described as “not energy efficient”. Of course, we can do better with thin film solar cells and this is a driving force to work on these types of solar cell. If you can do better, it doesn't mean that Si is bad or not efficient. We should not bash other PV technologies.

Jens Wenzel Andreassen answered: We fully agree that we should not bash other PV technologies. We fully acknowledge the benefits of crystalline Si PV in many aspects, and myself and several co-authors are running research on many technologies from kesterites to perovskites and crystalline Si. However, we do not consider it “bashing” to state that Si *production* is not efficient: energy and material consumption is very high (in particular purification with the distillation/Siemens process), and most thin-film technologies are better in that respect. Yet, that is currently almost the only advantage of thin-film technologies: as we state, new generations have to become competitive in terms of stability, upscaling, and energy payback time. This implies that they are not competitive in this respect today. The lower lifetime of many thin film devices leads to a reduced energy return on energy invested. Still, the energy payback time can be better than for crystalline Si. In a paper about ecological impact, these aspects would need to be elaborated on, but for a paper about a thin-film technology, we think our short version is appropriate.

Jonathan J. S. Scragg added: On the subject of motivating thin film research. I agree that we ought to be careful if making negative statements about existing Si-based PV technology. Instead, we can use the positive angle that a thin film based technology could *further* improve the energy and/or materials efficiency of PV.

Mirjana Dimitrievska stated: It is important for the emerging PV community to not compete directly with Si PV technology. We need to either work together with Si (tandems) or find new niche markets where Si doesn't work so well (flexible and transparent PV). Si PV has been there for more than 50 years, it would be very difficult to beat such technology, no matter how good a material we have.

Jens Wenzel Andreassen replied: If the motivation for research in thin film solar cells should not be the competition with silicon solar cells, what do you think it should be?

Mirjana Dimitrievska answered: Thank you for the interesting remark. I think that thin film solar cells have so much more potential in the uniquely identified areas of applications, where Si-based solar cells cannot compete or are not suitable. For example, flexible, lightweight or transparent solar cells are something that thin film materials will excel at. These can be used for everything from zero-energy buildings to smart sensors for the Internet of Things to e-textiles for device charging on-the-go. Additionally, rather than competing with Si, it is actually

much better to work with it, and find materials that will work well for tandem solar cells. This is my motivation to work on thin film PV.

Rafael Jaramillo addressed Jens Wenzel Andreasen and Charles J. Hages: What specifically is the role of zinc oxide in these devices? You have the perfect sample/model to address this question.

Jens Wenzel Andreasen addressed Charles J. Hages and Rafael Jaramillo: You are right, it would be an idea to try to test the performance through modification of the model parameters of the ZnO layer. I think this question was in response to the question by Rafael Jaramillo, on the function of the ZnO layer in kesterite solar cells.

As I remember, I phrased my answer as a question to the audience: is it what is sometimes called a hole blocking layer? I guess it is more commonly referred to as a “window layer” which helps prevent surface recombination of charges created in the top of the absorber layer.

Charles J. Hages responded: In our experience, the ZnO layer is predominantly responsible for forming the p–n junction (rather than CdS). For instance, no charge separation effects can be measured with CZTS/CdS, though they can for CZTS/CdS/ITO (*via* time-resolved photoluminescence).

Rafael Jaramillo added: I think this layer can play an important role in recombination management, in the details of the electrostatics of the junction (its photoconductivity can be important here). I think this layer can also help to prevent shunting of the transparent contact through to the absorber, and can also be processed differently from the transparent contact and thereby reduce sputter damage. I feel as if I've never fully understood the particular benefits of this layer, for any particular solar cell.

Byungha Shin asked: Hard X-ray would mostly produce photoelectrons from core levels, leaving holes bound to the core and therefore immobile. The relaxation (*i.e.*, filling of holes in the core levels) would give out a fluorescence signal, XRF. I would think the chances of producing free electron–hole pairs (*i.e.* excitation of valence electrons) are very slim by hard X-ray and expect the XBIC signal is very weak. Where are XBIC signals coming from?

Jens Wenzel Andreasen answered: During XBIC measurements of solar cells, the incident X-ray photons set off particle showers consisting of electrons and photons, resulting in a multitude of excited electron–hole pairs per incident X-ray photon in the semiconducting absorber material. These secondary excited electron–hole pairs thermalize to the band edges of the solar cell absorber and can thus be treated like charge carriers that are generated by the absorption of photons with energies just above the bandgap during normal solar cell operation. The resulting current or voltage can be measured as an X-ray beam induced current, similar to more common measurements like electron-beam induced current (EBIC) or laser-beam induced current (LBIC).

See also ref. 1.

1 C. Ossig, T. Nietzold, B. West, M. Bertoni, G. Falkenberg, C. G. Schroer and M. E. Stuckelberger, *J. Vis. Exp.*, 2019, **150**, e60001.

Thomas P. Weiss commented: You only have a 1 μm thick lamella but two (the front and back side of the cross section) free surfaces, which potentially add with a large surface recombination velocity to the different recombination channels.

Did you ever take these surface recombination components into account for your model/simulation?

Have you for instance measured a dark current–voltage characteristic of the thin lamella to see if the solar cell still has reasonably good rectifying behavior (and is not shunted by the free surfaces)? An improvement could be the deposition of a thin ALD Al_2O_3 passivation layer. The Al_2O_3 layer has negative charges and therefore repels electrons (minorities) from the surface. Consequently you would rather probe bulk properties.

An example of that approach is described for EBIC measurements by Bissig *et al.*¹

1 B. Bissig, C. Guerra-Nunez, R. Carron, S. Nishiwaki, F. La Mattina, F. Pianezzi, P. A. Losio, E. Avancini, P. Reinhard, S. G. Haass, M. Lingg, T. Feurer, I. Utke, S. Buecheler and A. N. Tiwari, *Small*, 2016, **12**(38) 5339.

Jens Wenzel Andreasen answered: The FIB'ed surfaces were not taken into account in the simulations, nor do we have I – V curve measurements. However, one of the co-authors does remember having checked the V_{oc} at ambient light prior to the XBIC measurement to check that the cell was not entirely shunted, but this was a quick-and-dirty multimeter measurement far away from controlled standard conditions. As an (unsatisfying) indication concerning shunts: if the cell had been badly shunted, the XBIC measurements had not been working properly. Also, surface passivation gets more important for low bulk recombination. For the studied CZTS cell, we're afraid that bulk recombination was dominant. However, the approach of depositing an Al_2O_3 layer on the free surfaces is an interesting suggestion and we will consider it for future measurements.

Nevertheless, we would prefer to perform this kind of study in 3D, where the free surfaces should have a minor impact compared to the bulk.

Thomas P. Weiss asked: What is the generation profile in an XBIC measurement?

How does it need to be taken into account when measuring thicker lamella or more bulk-like probes?

Jens Wenzel Andreasen replied: We could have added the generation profiles in the publication, we just did not consider them important enough as similar profiles have been published before. Obviously, we still have them and are happy to share the results of the Monte-Carlo simulations, by contact to the corresponding author of our article (<https://doi.org/10.1039/d2fd00044j>). In short, at the used energies, the beam is pencil-like throughout the sample thickness, lateral scattering is minimal. Similar simulations (not for CZTS but for perovskites; the results are comparable) are published *e.g.* in ref. 1–3. For bulk-like probes, the decreasing generation profile deeper in the material does in principle need to be taken into account if low energies or thick absorber materials are

used. However, for photon energies above 10 keV and thin-film devices (less than 2 μm CIGS/CZTS/perovskite) or less than 200 μm Si, the absorbance is comparably low and the profile may be considered constant in analogy to the red-light limit in the VIS case (we'll be happy to provide simulations for specific cases).

- 1 M. Kodur, R. E. Kumar, Y. Luo, D. N. Cakan, X. Li, M. Stuckelberger and D. P. Fenning, *Adv. Energy Mater.*, 2020, **10**, 1903170.
- 2 M. Stuckelberger, T. Nietzold, G. N. Hall, B. West, J. Werner, B. Niesen, C. Ballif, V. Rose, D. P. Fenning and M. I. Bertoni, *J. Photo.*, 2017, **7**, 590.
- 3 M. E. Stuckelberger, T. Nietzold, B. M. West, Y. Luo, X. Li, J. Werner, B. Niesen, C. Ballif, V. Rose, D. P. Fenning and M. I. Bertoni, *J. Phys. Chem. C*, 2020, **124**(33), 17949.

Hasan Arif Yetkin continued the discussion of the paper by Rafael Jaramillo: How did you understand or calculate that chalcogenides are covalently bonded?

Rafael Jaramillo responded: The basic expression for the ionic bond fraction $1 - \exp[-(\Delta\chi)^2/4]$, shows that Zr-S bonds are 32% ionic, which is not very ionic. We have studied the shape of the Zr-S bonds in $\text{Ba}_3\text{Zr}_2\text{S}_7$ in some detail¹ and we find features very typical of covalent molecular bonds. But, it's definitely open to interpretation!

- 1 K. Ye, N. Z. Koocher, S. Filippone, S. Niu, B. Zhao, M. Yeung, S. Bone, A. J. Robinson, P. Vora, A. Schleife, L. Ju, A. Boubnov, J. M. Rondinelli, J. Ravichandran, and R. Jaramillo, *Phys. Rev. B*, 2022, **105**, 195203.

Jonathan J. S. Scragg commented: Some different comments were made with respect to the covalency or ionicity of chalcogenide perovskites; at one point you referred to them as "covalent". I understand that you are using the (more ionic) oxide perovskites as a reference, but it is worth noting to this community that chalcogenide perovskites are substantially less covalent/more ionic than the materials we are used to, *i.e.* tetrahedrally bonded chalcogenides.

Rafael Jaramillo replied: Hi Jonathan, good point. I do venture that the electronic structure, the high mobility that we infer from TRPL and IR reflectivity, and the Pauling bonding rules for Zr-S bonds, all suggest substantial covalency. There is also a useful comparison with oxides and halides. Finally, the "surprising" trend in bandgap with layer number – and what I predict to see experimentally with the bandgap depending sensitively on octahedral tilts at twin and grain boundaries – all highlight the fact that covalent bonding is important for the semiconducting properties and performance.

All that said – yes, Si, ZnS, GaAs, ... are more covalent!

David B. Mitzi asked: On slide 3 or 4 of your presentation, a large array of prospective (theory-predicted) chalcogenide-based perovskites is shown (the figure is from ref. 1), yet relatively few of these have been reported synthetically, *i.e.*, most are based on hafnium or zirconium as the metal. Is there something fundamental about chalcogen-based chemistry that makes it more difficult to stabilize chalcogenide-based perovskites (relative to, for example, oxides or halides), or is the relative rarity of these structures more related to synthetic challenges or just the early stage of the field?

- 1 R. Jaramillo and J. Ravichandran, *APL Mater.*, 2019, **7**, 100902.

Rafael Jaramillo replied: Hi David, I think the challenge is mostly simply understood as stemming from the tolerance factors. A secondary effect may be that S and Se like to bond with themselves, so perhaps this is a driving force to the formation of layers and chains, with higher S–S and Se–Se coordination. I don't have an up-to-date survey of all of the experimental attempts to make this list of materials, and of the outcomes. I wish I did, that would be interesting; especially for the low bandgap (MWIR) predicted materials, I find them very intriguing, but my own group doesn't have the bandwidth or really the expertise to do the needed solid state synthesis well.

David B. Mitzi continued: If we can understand what factors make the stabilization of chalcogen-based perovskites more challenging, then I wonder whether this understanding could be used to help stabilize the phases, such as through the use of epitaxy with a substrate or use of strain effects?

Rafael Jaramillo replied: Hi David, yes indeed. For our high-Se content films (including BaZrSe₃), we know that epi growth is important. We don't know where in the BaZrS₃–BaZrSe₃ phase diagram the perovskite phase becomes unstable, that is an interesting open question. Professor Hages was musing about finite-size stabilization in nanocrystals, and perhaps also core–shell type structures. Further suggestions and results are most welcome!!

David J. Fermin asked: Your TRPL studies focus on phase pure materials, which is crucial for assessing the potential of this new class of materials for PV applications. However, when considering conventional processing of thin-film devices, one would expect the presence of a mixtures of phases. Have you performed experiments in materials exhibiting a mixture of phases? Would secondary phases severely compromise the optoelectronic properties of this perovskite chalcogenide? Which phase would be the most detrimental?

Rafael Jaramillo answered: Hi David, our powders and crystal samples (made by Ravichandran's group, USC) are pure phase, as best we can tell.

The S–Se alloy films have more detail. The Se alloys are made on a BaZrS₃ buffer layer. They grow pseudomorphically in the perovskite structure, so that crystal motif is consistent, but we do have the two-layer structure by design. At high Se content, we start to see Se segregation, laterally, resulting in composition (and necessarily bandgap) variations in 3 dimensions. Because of these complications, we have limited our optical measurements to the single-composition, single-phase samples. The alloy samples we have instead studied with photocurrent/devices, microscopy, AFM, *etc.* Another complication: when we try to grow the crystal fast, the e-beam arcs too often, throwing off our metal ratios. This leads to extended defects, as is long known in the oxide perovskite field. This is an equipment issue, not an intrinsic materials issue. But it's an issue for us nonetheless.

I will add: we have been using very high substrate temps, simply because we're following oxide MBE protocols. At thermocouple temps at 900 °C and above, the growing film surface is probably in the 700–800 °C range (hard to know for every growth run). So, it's unsurprising to see S/Se diffusion. Lots of opportunity in

reducing the growth temp, which is on our to do list, we just haven't gotten around to it.

Seán R. Kavanagh asked: In the final paragraph of your results section, you suggest that the mobility is limited by defect scattering all the way up to room temperature. Do think that is indicative of very large defect concentrations in these materials, or perhaps due to unusually low phonon scattering, or other effects?

Rafael Jaramillo answered: Hi Sean, yes, I remember that now – I was confused by the question at the meeting, and I'm sorry for contradicting myself! The observation was based on the weak temperature dependence of the mobility, calculated from the diffusivity data inferred from the TRPL modeling. Phonon-scattering models have stronger temp. dependence.

My opinion: it's a bit early to frame a particular hypothesis well enough for it to be worthwhile pursuing in theory. I think more data, and particularly temp. dependent Hall (soon, I hope!!), will clarify things and create more incentive.

Young Won Woo remarked: In your paper, you tested the trend of bandgap vs. T below 300 K for $\text{Ba}_3\text{Zr}_2\text{S}_7$. Did you find a similar trend for BaZrS_3 ? And I wonder if you also tried higher temperatures (above 300 K)?

Rafael Jaramillo answered: Good question, thank you. We don't have trend data for BaZrS_3 , yet. We also don't have higher temp data for the simple reason that the cryostat couldn't heat much above room temp. Gross *et al.* published nice data on BaZrS_3 at high pressure:¹ they found the bandgap decreases with pressure. So, if this means that a smaller unit cell decreases the bandgap, then perhaps thermal expansion would increase the bandgap? Just a guess.

1 N. Gross, Y.-Y. Sun, S. Perera, H. Hui, X. Wei, S. Zhang, H. Zeng and B. A. Weinstein, *Phys. Rev. Applied*, 2017, 8, 044014.

Prakriti Kayastha asked: $\text{Ba}_3\text{Zr}_2\text{S}_7$ in the $P4_2/mnm$ has been shown as the low temperature polymorph. In your paper you show that your experiments take place >1000 °C. Do you see the $\text{Ba}_3\text{Zr}_2\text{S}_7$ in the $I4/mmm$ phase? Follow up: in publicly available databases the bandgap of the $\text{Ba}_3\text{Zr}_2\text{S}_7$ in the $I4/mmm$ phase (0.51 eV evaluated with PBE from AFLOW) is smaller than the bandgap of $\text{Ba}_3\text{Zr}_2\text{S}_7$ in $P4_2/mnm$ (0.83 eV from AFLOW). Is there a bandgap dependency you see in your work with temperature change/phase change (if there is one)?

Rafael Jaramillo replied: The synthesis temp is 1050 °C, and the crystals do form in the low-temp. polymorph. All of our property measurements are at room temp. and below. We don't have any measurements in the $I4/mmm$ phase, maybe there are other groups that have published measurements on this phase? I'm curious if there are.

The bandgap trend with structure was studied theoretically in some detail by Janotti and Ravichandran:¹ you'll see predictions for different structures, including $I4/mmm$. It's interesting!

1 W. Li, S. Niu, B. Zhao, R. Haiges, Z. Zhang, J. Ravichandran and A. Janotti, *Phys. Rev. Materials*, 2019, 3, 101601.

Christopher Savory communicated: This was some fascinating work, particularly on the Ruddlesden–Popper phase – I just wanted to ask a question regarding the peak-splitting in the PL emission of $\text{Ba}_3\text{Zr}_2\text{S}_7$, tentatively assigned to the exciton binding energy. While 17 meV would be on par with the halide perovskites, the calculated band structure of $\text{Ba}_3\text{Zr}_2\text{S}_7$ is very different from that of the 3-dimensional halide perovskites, with a relatively flat valence band and effectively no dispersion in the conduction band along the layer stacking direction.¹ Overall, we might expect much lower carrier effective masses, closer to those of the 2D layered halide perovskites – is the hypothesised weak exciton binding purely coming from high dielectric screening? Is there also more that photoluminescence can tell us about the excitons in this material?

1 S. Niu, D. Sarkar, K. Williams, Y. Zhou, Y. Li, E. Bianco, H. Huyan, S. B. Cronin, M. E. McConney, R. Haiges, R. Jaramillo, D. J. Singh, W. A. Tisdale, R. Kapadia and J. Ravichandran, *Chem. Mater.*, 2018, 30, 4882–4886.

Rafael Jaramillo communicated in reply: Yes, the hypothesis is based purely on the low frequency dielectric response, that we reported previously.¹ It's really just a suggestion, and I'm open to other suggestions and especially more and different data! In particular, low-temp. PL on numerous different crystals, ideally prepared by different labs, would go a long way. But it seems the field isn't there yet.

1 A. Singh, S. S. Jo, Y. Li, C. Wu, M. Li and R. Jaramillo, *ACS Photonics*, 2020, 7(12), 3270.

Conflicts of interest

There are no conflicts to declare.