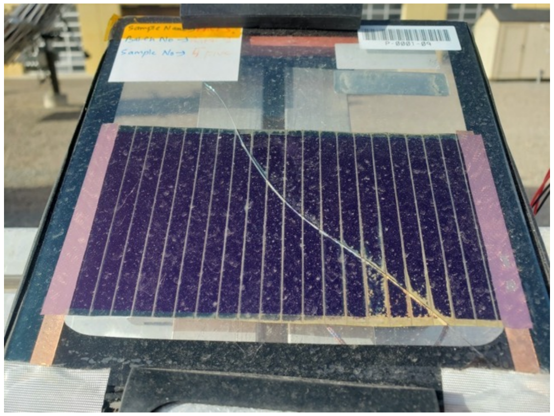
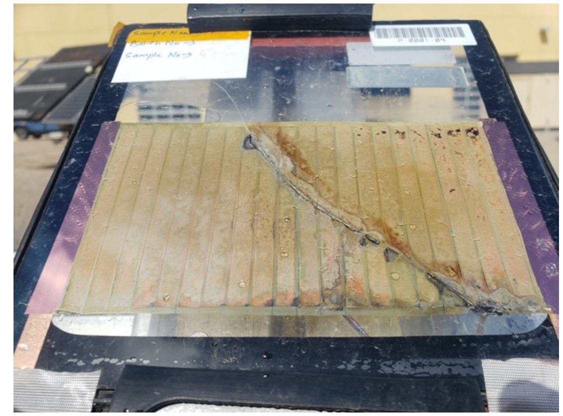




IEA PVPS

Perovskite and tandem degradation challenges and mitigation strategies

Joshua S. Stein PhD. (Sandia), Sara Baumann (ISFH), Mark Khenkin (HZB)

Content also from Giles Eperon (Swift Solar) & Laura Mundt (Stanford University) – "Perovskite failure modes: What do we know so far?" PVQAT Talk November 2, 2021.

October 6, 2022 Frankfurt am Main, Germany, Degradation modes in new PV cell & module technology

Technology Collaboration Programme by iea

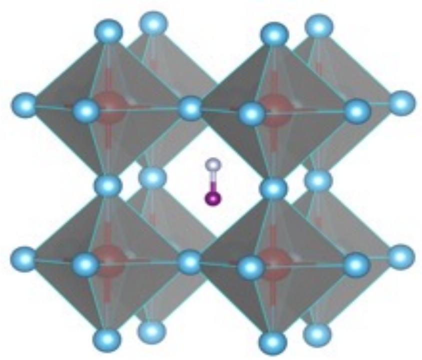
SAND2023-10479C

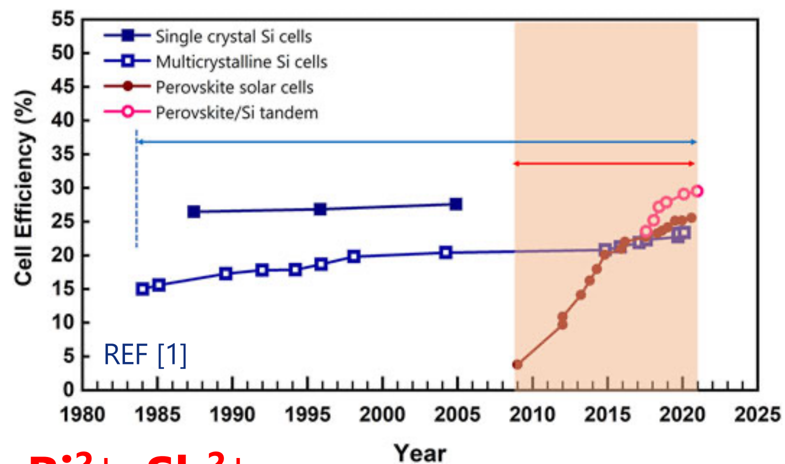
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Perovskite PV Introduction

- “Perovskite” refers to crystal structure
- Metal Halide Perovskite PV has a range of chemical compositions:

ABX_3





A= Pb^{2+}, Sn^{2+}, Ge^{2+}, Bi^{2+}, Sb^{2+}, …

X=Halides (Cl^-, Br^-, I^-)

B= Organics or metal (Cs^+)

History

- First perovskite PV cell made in 2009
  - <3% PCE (power conversion efficiency)
- PCE has risen fast
  - >= 25.6% today at the cell level (limit – 33%)[1]
  - It took 40 years to achieve this PCE for c-Si.
- Promise of low cost manufacturing
  - Low temperature
  - Solution processing
  - High speed manufacturing

[1]Zhang et al., 2022: 10.3389/fchem.2022.802890

Degradation Modes for Perovskite PV

Perovskite PV materials are characterized by:

- **Weak bonds** allowing ions to move around in response to electric fields
- Susceptibility to degradation when exposed to **moisture**, **oxygen**, **heat & light**.

Packaging needs to **keep water out** and gasses (from heating) inside[1].

- Outgassing reactions are reversible.

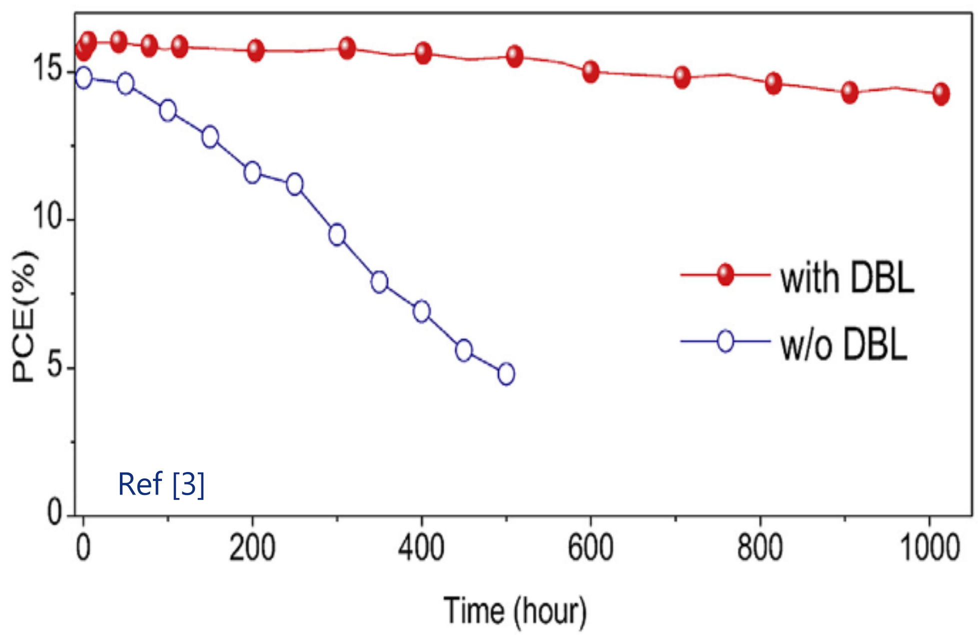
Degradation Mode Classification:

- **Extrinsic** (water, oxygen, mechanical stress, potential induced degradation)
- **Intrinsic** (phase instability, halide segregation, decomposition)
- **Device specific** (electrode diffusion, transport layer reactions, reverse bias)

[1]Shi, L. *et al. Science* **368**(2020).

Extrinsic: Water

Protection against humidity by a diffusion barrier



- Formation of PbI_x[1]
- Can be solved by glass-glass modules[2], sputtered barriers[3,4] or back-/frontsheets with diffusion barriers and edge sealing[2]
- Several reports on modules that withstand damp heat tests for at least 1000 h (IEC 61646)[2,5]

[1]Yang et al., ACS Nano 9, 1955-1936 (2015)
[2]Cheacharoen et al., Sustainable Energy Fuels, 2, 2398 (2018)
[3]Bi et al., Joule 3, 2748-2760 (2019)
[4]Ahangharnejhad et al., ACS Appl. Energy Mater., 4, 7571-7578 (2021)
[5]Azmi et al., Science, 376, 6588, 73-77 (2022)
[6]Arias-Ramon et al., Solar Energy Materials and Solar Cells, 215, 110625 (2020)

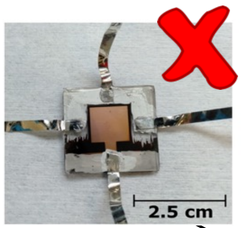
PVPS

Mitigation: good encapsulation (diffusion barriers, edge seals, hydrophobic additives)[6]

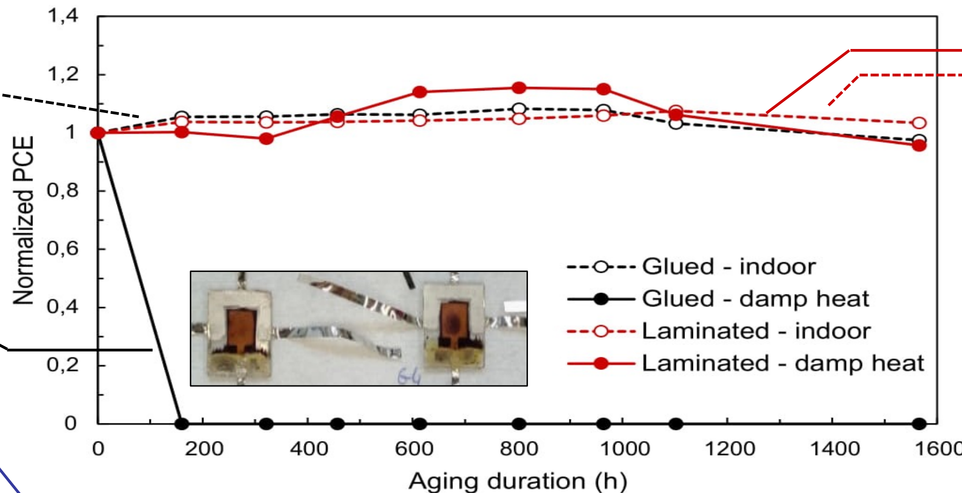
Slide content from Sara Baumann, ISFH

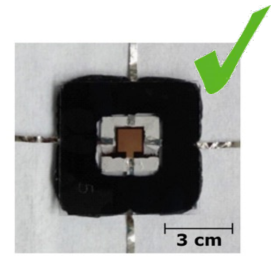
Packaging Examples

DAMP HEAT TEST



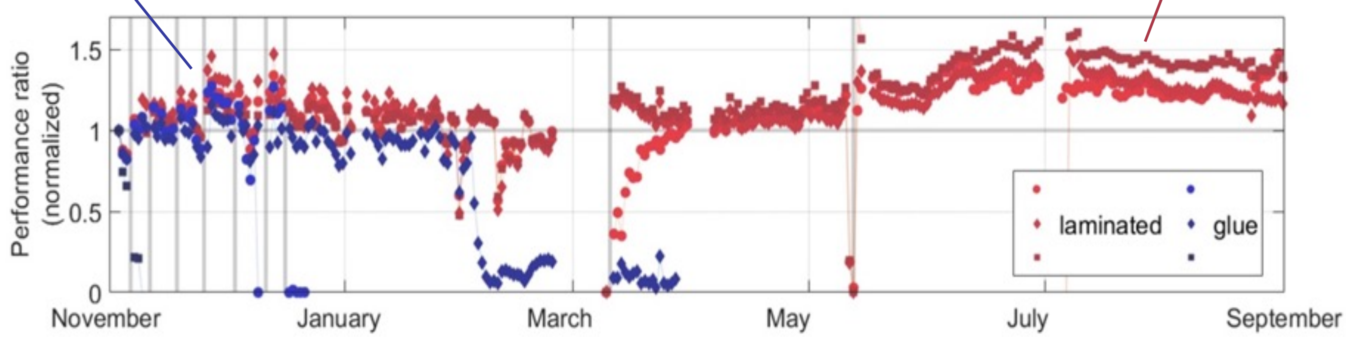
"Glued"





"Laminated"

OUTDOOR



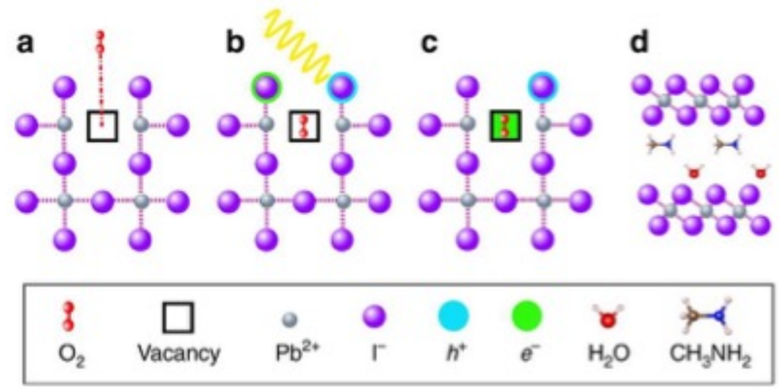
PVPS

Emery et al., ACS Appl. Mater. Interfaces 2022, 14, 4

Slide content from Mark Khenkin, HZB

Extrinsic: Oxygen

- Lead-halide perovskites: oxygen reacts with the perovskite under light.
  - MAPI forms superoxides in iodide defect sites.
- Tin perovskites: oxygen oxidises the tin.



Reaction is unfavorable without light

$$4CH_3NH_3PbI_3 + O_2 \rightarrow 4PbI_2 + 2I_2 + 2H_2O + 4CH_3NH_2$$

With light, O_2 gathers free electrons and forms a superoxide (O_2^-)

$$4CH_3NH_3PbI_3^* + O_2^- \rightarrow 4PbI_2 + 2I_2 + 2H_2O + 4CH_3NH_2$$

Aristidou, *Nat. Com.* 2017

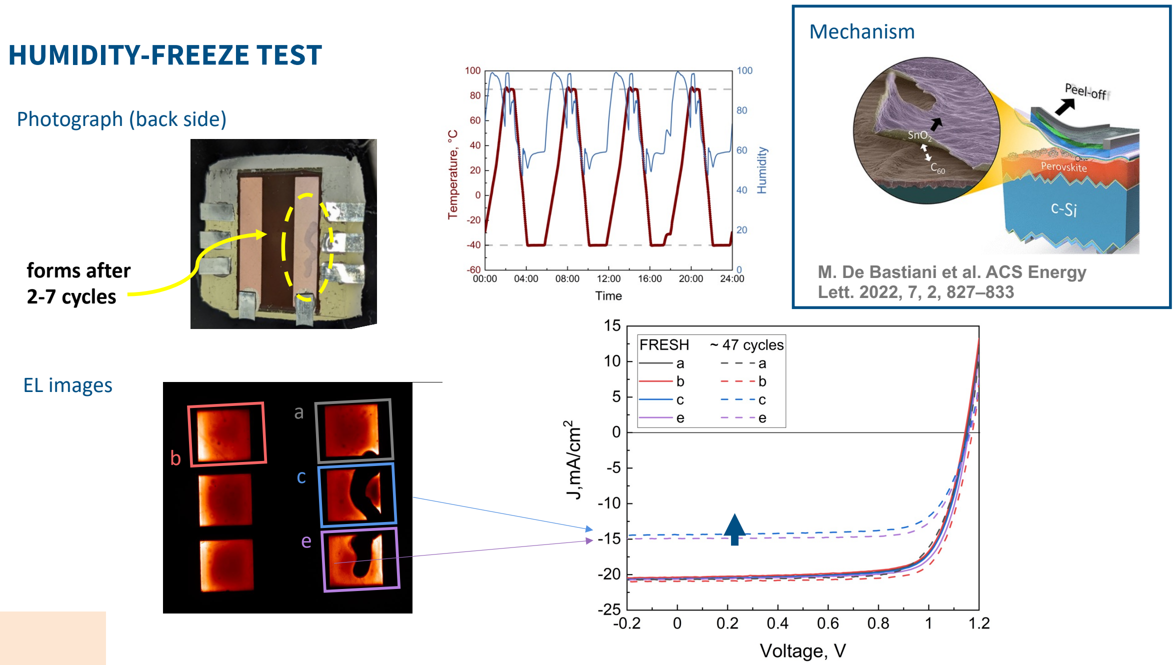
PVPS

Mitigation: good encapsulation, cell design with efficient charge extraction, larger perovskite crystals

Extrinsic: Mechanical Stress

- Mechanical instability of perovskite materials can cause:
  - Issues with delamination
  - Challenges with establishing good electrical contacts
  - Dissimilar thermal expansion coefficients cause stress during thermal cycling
- External stress from wind, hail, snow.

Example of Mechanical Degradation



U.Erdil et al., HZB, in preparation

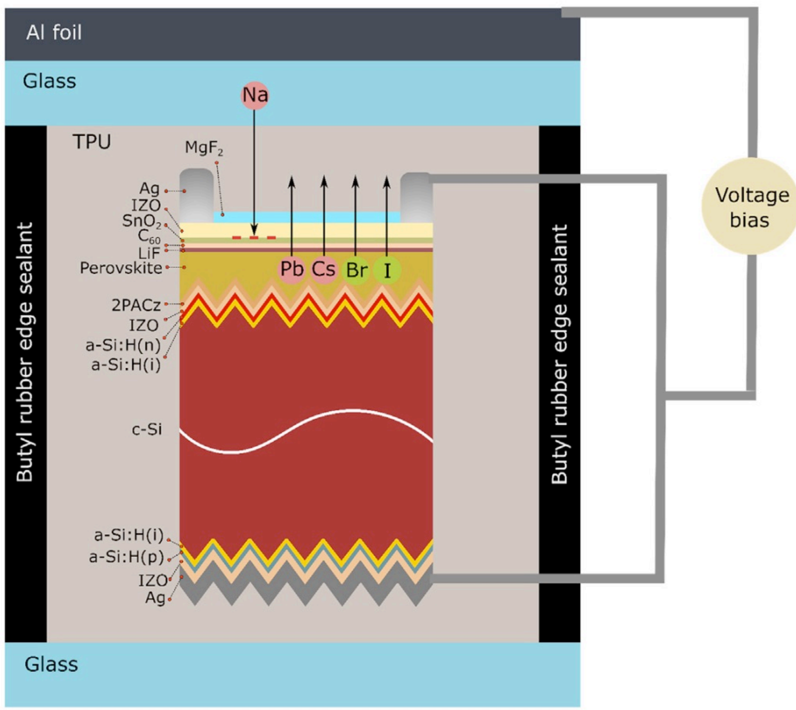
PVPS

Mitigation: Matching CTEs for materials, robust packaging, ample testing.

Slide content from Mark Khenkin, HZB

Extrinsic: Potential Induced Degradation

c



Xu et al.,Cell Reports Physical Science 3, 101026 (2022)

PVPS

Mitigation: select encapsulant with lower diffusion rates (e.g., POE), other barrier layers

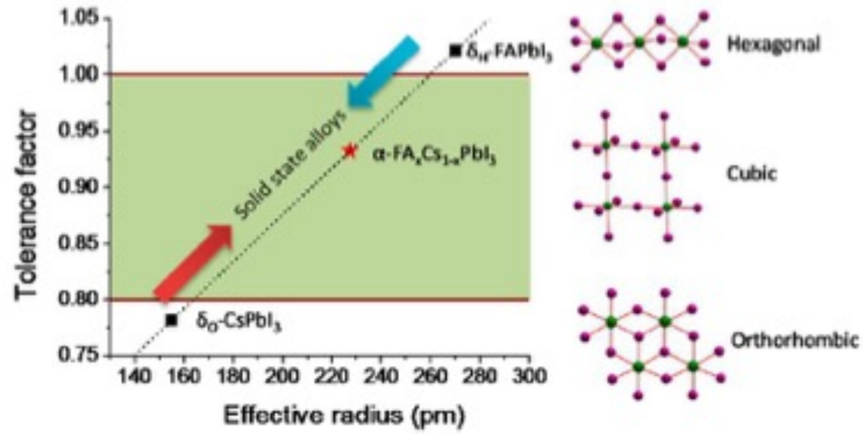
Requires bias + heat

- -1000 V applied for 1 d @ 60 °C to tandem module => 50% PCE loss
- No obvious shunts, Na^+ ions from glass confined above cells (EDX)
- Diffusion of perovskite elements into encapsulant
- SIMS profile show Cs, Pb, Br and I, as negatively charged ion groups, diffuse along electric field
- Pos. voltage can partially recover PID
- Barriers to prevent diffusion might me needed for commercialization

Slide content from Sara Baumann, ISFH

Intrinsic: Phase Instability

- Depending on A-site cation selection or mixture, perovskite can be unstable in photo-active crystal phase at room temperature. Phase change to delta/yellow phase can happen over long timescales in $FAPbI_3$.



Li et al., *Chem. Mater.* 2016
Schelhas et al., *EES* 2019

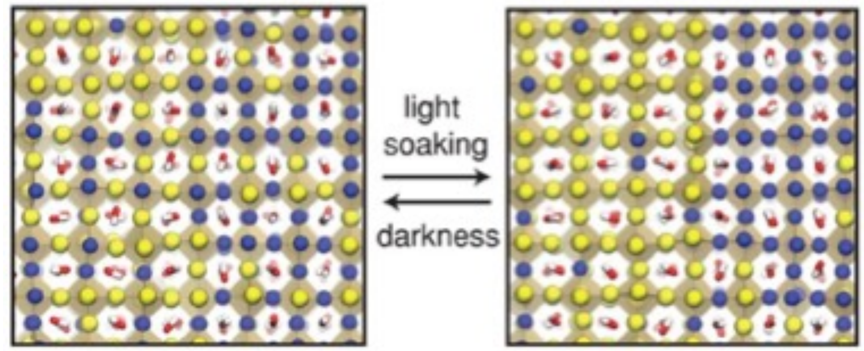
Mitigation: choose a composition that's in the phase stable regime - note that this space has not been fully explored for all variations of perovskite components yet!

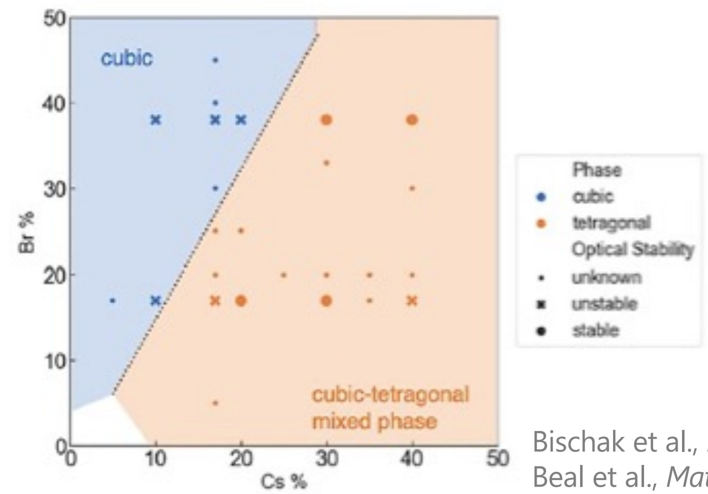
PVPS

Slide content from Giles Eperon (Swift Solar) & Laura Mundt (Stanford University)

Intrinsic: Halide Segregation

- Under illumination, perovskite compositions with halide ratios (normally I:Br) in a certain regime will undergo halide segregation, limiting voltage and creating defects.





Bischak et al., *Nano Lett.* 2017
Beal et al., *Matter* 2020

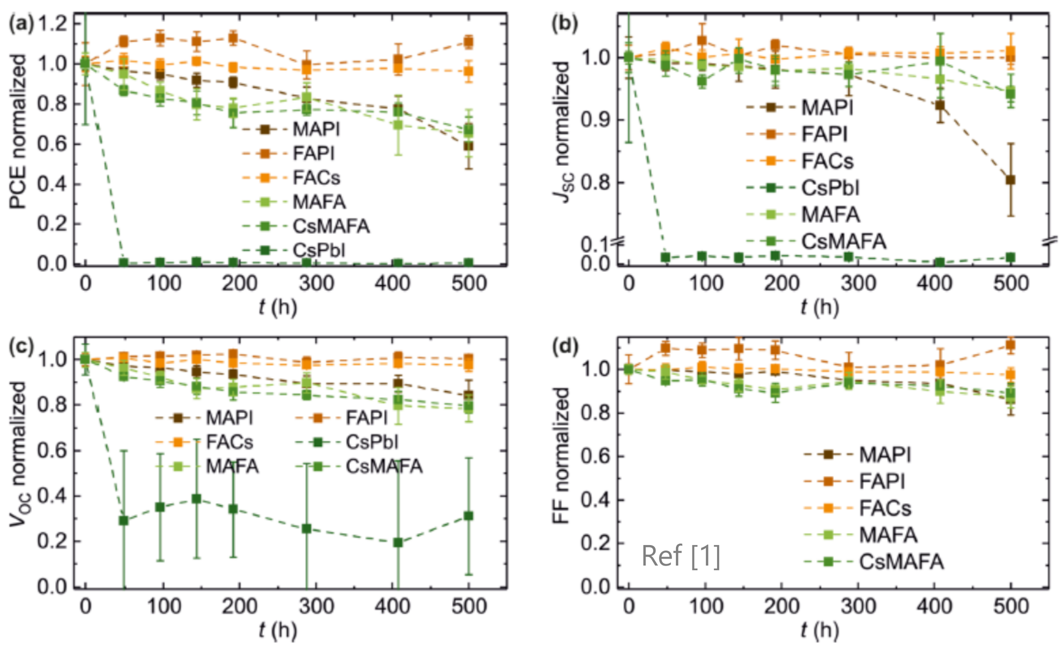
Mitigation: choose a composition that doesn't segregate but also depends on A-site and B-site.

PVPS

Slide content from Giles Eperon (Swift Solar) & Laura Mundt (Stanford University)

Intrinsic: Thermal Decomposition

Thermal stability at 85 °C in nitrogen of different perovskite compositions



PVPS

Mitigation: Addition of heat dissipation material (e.g., silicon dioxide particles at perovskite/HTL interface)[5]

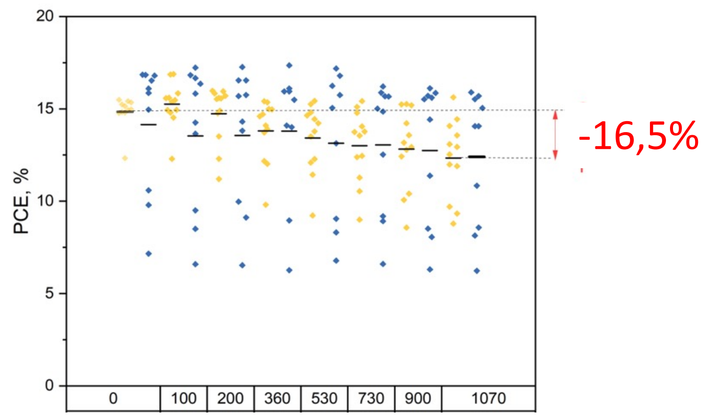
- Solar cells need to withstand high temperatures during module fabrication (typically > 100 °C) and operation (> 65 °C) [2]
- $MAPbI_3$ decomposition (resulting in PbI_2 among others) starts at 85 °C even under air free conditions[1,3,4]
- Perovskites containing MA less thermally stable than $FAPbI_3$ and $FACsPbI_3$[1]

[1]Schwenzer et al., ACS Appl. Mater. Interfaces, 13, 15292-15304 (2021)
[2]Raman et al., Renewable and Sustainable Energy Reviews 151, 111608 (20
[3]Conings et al., Adv. Energy Mater., 5, 1500477 (2015)
[4]Kim et al., Scientific rports, 7, 4645 (2017)
[5]Pei et al., ACS Energy Lett., 6,9, 3029-3036 (2021)

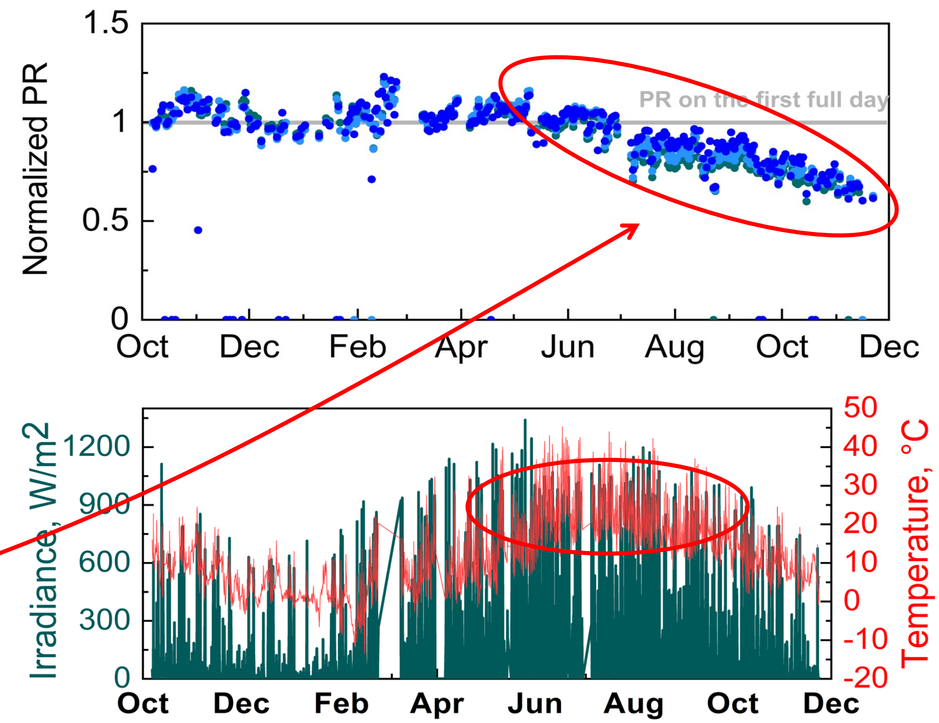
Slide content from Sara Baumann, ISFH

Thermal Degradation Examples

DAMP HEAT TEST



OUTDOOR



Weak (-ish) thermal stability translates into degradation in summer

J.Li et al., HZB, submitted

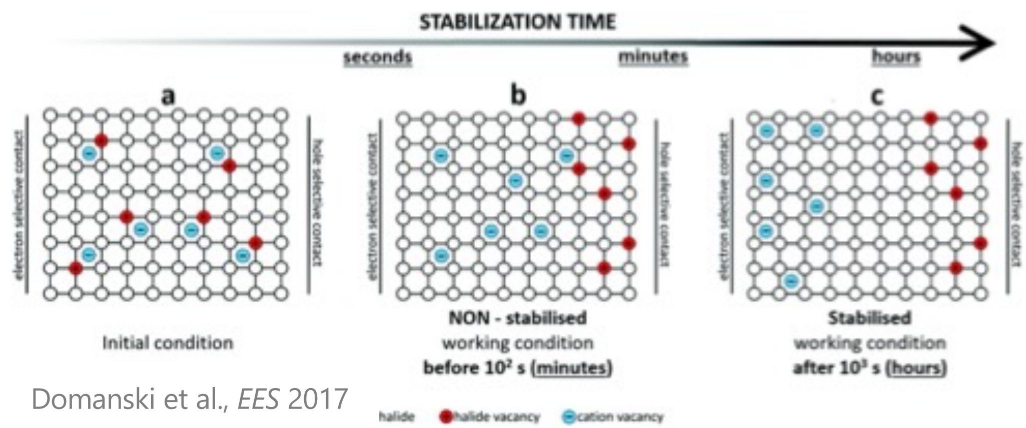
PVPS

Slide content from Mark Khenkin, HZB

Intrinsic: Ion Migration

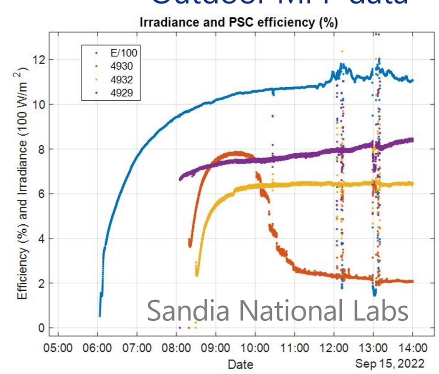
- The constituents of the perovskite lattice (A, X and even B) are able to migrate under low energy inputs
- Mobile ions (most likely iodide) likely shuffle back and forth over day/night cycling.
- Any changes are likely mostly reversible (‘morning recovery’ has been observed with some stacks), unless there is a reaction between mobile ions at one interface.

Mitigation: reduce diffusivity



Domanski et al., *EES* 2017

Outdoor MPP data



Recovery?

One module fails rapidly

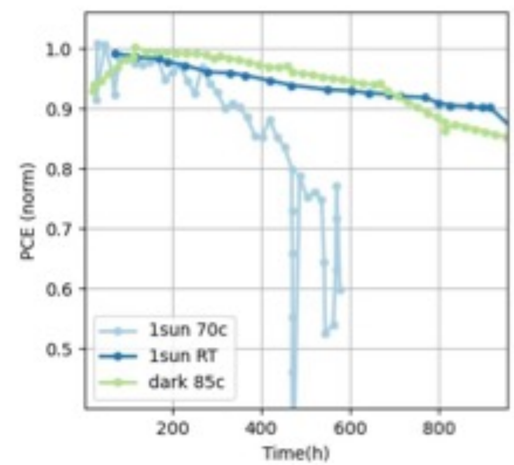
PVPS

Slide content from Giles Eperon (Swift Solar) & Laura Mundt (Stanford University)

Device: Electrode Diffusion

- Common metals used for top electrode, and some TCOs, diffuse through the stack and react with the perovskite, forming things like AgI, Pb_0 or creating shunt paths.
- If components of the perovskite can diffuse out, they can react with the metal/TCO too.
- Likely more problematic at scribe lines in monolithically interconnected modules.
- This process will happen just under heating, but it is **accelerated dramatically by heat + light conditions** (e.g. operation under elevated temp).

<u>Considered to be one of the most challenging instabilities to make a cost-effective perovskite cell.</u>



Schulz et al., *Chem. Rev.* 2019; Kerner et al., *ACS Energy Lett.* 2020; Schmidt-Mende et al., *APL Materials* 2021

PVPS

Mitigation: Use non-metal electrodes (TCOs, carbon), diffusion barrier (e.g., ALD-SNO_x)

Device: Transport Layer Reactions

Various issues with certain HTL or ETL choices:

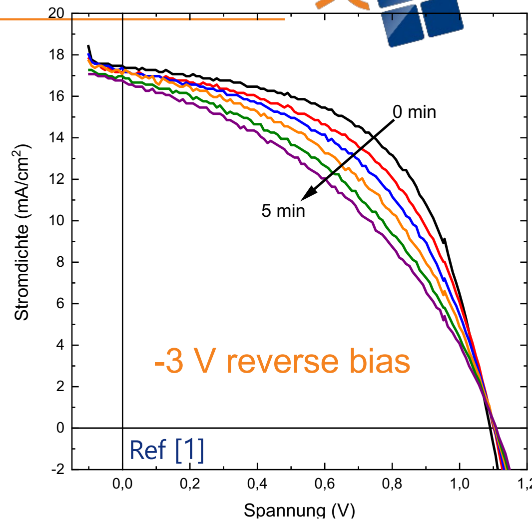
- Reaction with perovskite (e.g. ZnO, NiO, some dopants)
- Thermal instability (e.g. MoO_x, some organics)
- UV or photo-instability (TiO_2)
- Delamination issues

Mitigation: Selection of appropriate materials for HTL and ETL (e.g. SnO_x, V_2O_5, C_{60}, PTAA, polytpd, etc.)

Slide content from Giles Eperon (Swift Solar) & Laura Mundt (Stanford University)

Device: Reverse Bias

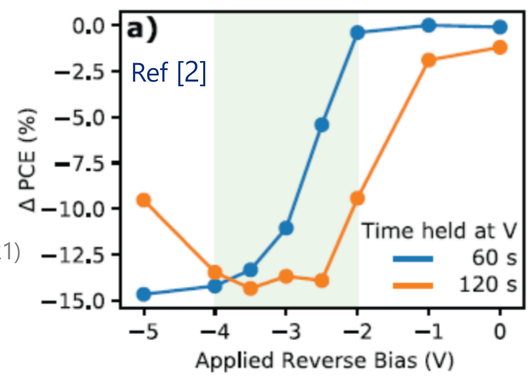
- Partial shading forces cells to operate under reverse bias
- Reverse bias leads to fast and partial irreversible degradation in V_{oc}, I_{sc}, *FF* & η[1]
- Breakdown differs from avalanche mechanism in cSi cells
- Degradation mechanism based on ion migration[2,3,4]



Mitigation: (1) Use carbon-based HTL[5],
(2) Avoid direct metal contacts[6],
(3) Avoid single-cation, single halide perovskites[6],
(4) include hole blocking layer between ETL and perovskite[7,8],
(5) new interconnection schemes and bypass diodes[9]

PVPS

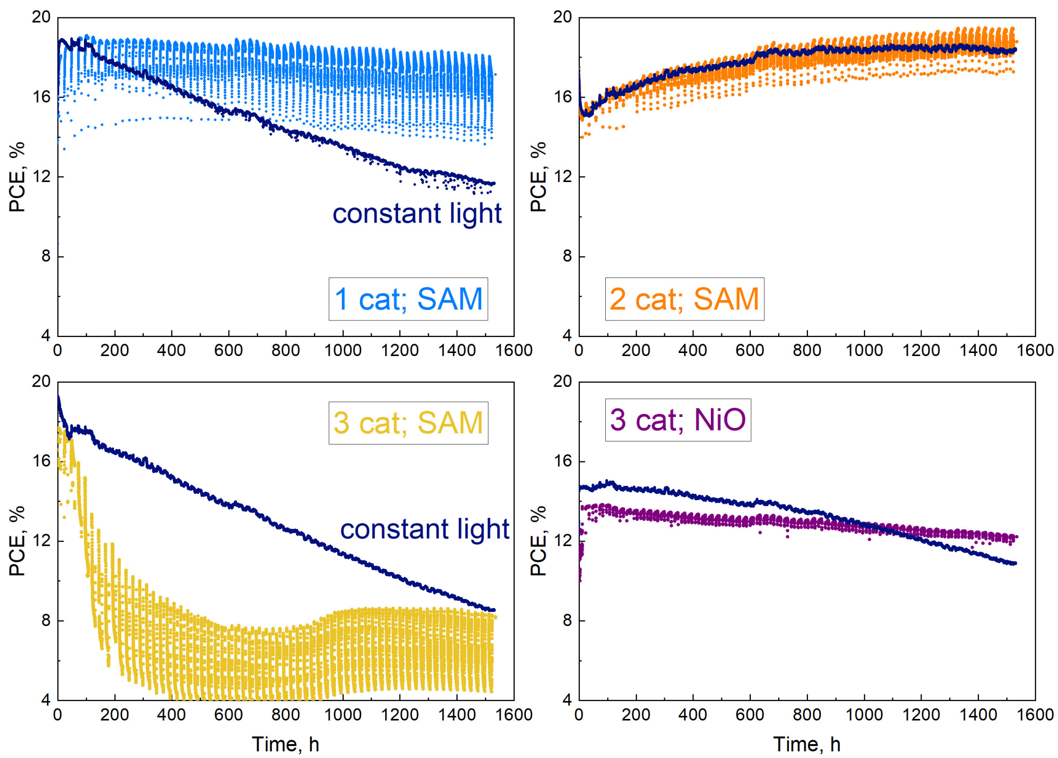
[1] Richter, master´s thesis, ISFH (2021)
[2] Gould et al., IEEE 48th PVSC, 21129020 (2021)
[3] Bertoluzzi et al., Adv. Energy Mater., 11, 2002614 (2021)
[4] Bowring et al., DOI: 10.1002/aenm.201702365 (2017)
[5] Bowering et al., Adv. Energy Mater. 8, 1702365 (2018)
[6] Bogachuk et al., Sol. RRL, 2100527 (2021)
[7] Gould et al., IEEE 48th PVSC, 21129020 (2021)
[8] Ni et al., Nature Energy, 7, 65-73 (2022)
[9] Wolf et al., Sol. RRL, 2, 2100239 (2021)



Slide content from Sara Baumann, ISFH

Metastability

- Affects short-term (within one day/cycle) and long-term stability.
- Not always in a positive way.
- Strongly dependent on the device architecture.
- Translates into the outdoor operation



M. Khenkin, H. Köbler et al., HZB, in preparation

PVPS

Slide content from Mark Khenkin, HZB

Summary

- Extrinsic, intrinsic and device-specific degradation modes have been summarized.
- Extrinsic modes can be mitigated with effective encapsulation
- Intrinsic modes can be mitigated by selecting the right composition, engineering to increase heat dissipation, and surface engineering.
- Device-specific modes can be mitigated by using non-metal electrodes, diffusion barrier materials, bypass diodes.
- Solutions must be able to scale in size and speed for production.
- More outdoor field tests are needed to identify relevant degradation modes.
  - Just because you can induce in a lab does not mean it will be a problem outside (e.g., diurnal and seasonal patterns)

www.iea-pvps.org

Joshua S. Stein, TASK13
jsstein@sandia.gov

IEA PVPS

Technology Collaboration Programme
by iea