PerTPV – Perovskite thin film photovoltaics

D5.6

Environmental Stressing

WP5

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Authors: OXPV, UOXF, CSEM
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Revision History

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Matt Klug, OXPV	Draft deliverable	28/09/2021
Matt Klug, OXPV	Revision 1	30/09/2021
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Contents

The PerTPV project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 763977.

1. Objective

The purpose of this deliverable is to report on the efforts taken within PerTPV to assess the reliability of perovskite single-junction and tandem devices. This is done by applying a series of environmental stressing conditions that align with the international photovoltaic (PV) module certification assessment criteria outlined in IEC 61215 by the International Electrotechnical Commission. The original goal was to perform the stressing testing within the consortium and then send laminates for external qualification once they had passed with less than 5% losses.

2. Introduction

With energy cost being one of the main drivers for any new renewable energy technology to be accepted at a global scale, levelised cost of electricity (LCOE) calculations are typically used to evaluate the cost competitiveness of a new technology. Such calculations have been performed in Deliverable D5.7 of the PerTPV project and examine how perovskite technology can compete based on its performance parameters and estimated cost metrics. For PV systems, however, solar cell durability and reliability are essential aspects that not only impact these cost calculations but will ultimately determine if a technology is competitive enough to deploy at a global scale.

Nowadays, most new solar device developers need to guarantee that their products will last for at least 25 years outdoors with less than 20% relative power loss, for them to be competitive against other energy technologies. For this reason, the industry has been looking for lab-based accelerated ageing methods aiming at mimicking outdoor module degradation modes. The IEC 61215 set of standards were designed by the International Electrotechnical Commission with the aim of disseminating such testing protocols, providing solar product manufacturers with a unified method to qualify their products.[1], [2] Other more comprehensive or harsher reliability qualification tests now exist but the IEC protocols remain some of the most used reliability standard tests in the PV industry and can consequently be used to determine the minimal reliability requirements for a new PV technology.

The IEC PV reliability protocols include various sequences of preconditioning and stressing tests, involving different mechanical, electrical and other physical environmental factors. They are designed to qualify the inherent stability of the solar cell and module materials against individual or combined stressing factors, but also to test the integrity and the protection level of the cell packaging (*i.e.*, encapsulation). These tests, such as damp heat, thermal cycling, humidity-freeze, and ultraviolet (UV) light exposure for example, are specifically designed to promote device degradation modes (diffusion, mechanical stress, moisture ingress, condensation, photo-ageing, etc.) that typically occur during their lifetime in the field.

Subjecting a new product to the full IEC pre-conditioning, test and stress sequences is a long and costly process. However, new devices can be subjected to a selection of the most relevant tests to gather quicker feedback on their stability and reliability. With perovskite-based devices being inherently sensitive to environmental triggers such as heat, humidity and light, particular attention should be paid to the test sequences involving these stress factors. Therefore, for this project, five environmental stressing tests were selected to be performed separately on devices encapsulated in glass-glass laminates. Four of them are from IEC 61215: damp heat, temperature cycling, humidity-

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freeze, and UV exposure. The fifth is not specified by the IEC standard but considers prolonged illumination under simulated sunlight while at elevated temperature. A short description and purpose of each test performed in this deliverable is presented in Table 1.

Table 1. Description of the environmental stressing tests performed

Test	Condition	Total Duration	Purpose
Damp Heat (DH)	(85±2)°C at (85±5)% RH	1000 hours	To determine the ability of the module to withstand the effects of long-term penetration of humidity.
Thermal Cycling (TC)	85°C/-40°C with at least 10 min dwell at max/min temperatures with 100°C/h ramps between	200 cycles	To determine the ability of the module to withstand thermal mismatch, fatigue and other stresses caused by repeated changes of temperature.
Humidity-Freeze (HF)	85°C (20 h dwell) at (85±5)% RH then 4 h interval without RH control where drop to -40°C (30 min dwell) and back	10 cycles	To determine the ability of the module to withstand the effects of high temperature and humidity followed by sub-zero temperatures. Note, this is not a thermal shock test.
UV Light Soak (UV)	Ultraviolet light exposure in range of 280-400 nm at (60±5)°C	15 kWh/m^2 dose	To subject the module to ultra-violet radiation to identify those materials and adhesive bonds that are susceptible to UV degradation.
Light Soak at Elevated Temperature (LeT) – *Not IEC	Exposure to simulated AM1.5G Sunlight while at 60°C	2000 hours	To determine the ability of the module to withstand continuous sunlight exposure at elevated temperature.

3. Devices

3.1 Solar Cell Devices

A set of fifteen nominally identical research sized single-junction solar cells with either a wide or a narrow band gap perovskite were prepared by the University of Oxford (UOXF). The selected compositions and band gaps correspond to those that were incorporated into each of the two sub-cells in the two-terminal tandem devices made by the consortium across the various work packages of this project.

The perovskite composition for the wide band gap devices is $(FA_{0.83}Cs_{0.17})Pb(I_{0.77}Br_{0.23})_3$ and was prepared using an ionic salt additive following the method reported previously.[3] The perovskite composition for the narrow band gap devices is $(FA_{0.83}Cs_{0.17})(Pb_{0.5}Sn_{0.5})I_3$ and was prepared using the method described previously.[4] Both device builds used polymer hole transport layers and Cr/Au metal electrodes in a p-i-n device configuration to avoid known instabilities associated with common hole transporters such as PEDOT:PSS or spiro-OMeTAD and silver electrodes.

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3.2 Lamination

To simulate a commercial solar module, encapsulation procedures were developed and implemented to laminate the devices prepared by UOXF between two pieces of glass. Because the narrow band gap perovskite degrades upon prolonged air exposure due to the well-known chemical instability of Sn^{2+}, which readily oxidises to Sn^{4+}, a procedure was developed to prepare and seal these laminates in an inert environment. Lamination was performed using industry standard materials for the edge sealant and encapsulant. Prior to encapsulating the UOXF devices, the encapsulation procedure was worked up and tested on bare substrates to confirm the integrity of electrical connections and minimise the chance of breakages occurring during the process.

Each of the solar cell device substrates from UOXF contains 4 electrically separated devices, or pixels, three with a 0.25 cm^2 active area and one with 1 cm^2. The 2-3 pixels with the highest efficiencies on each substrate were connected with tabbing wire to allow for photovoltaic performance measurements once encapsulated. Figure 1 shows a representative example of a laminated device when viewed from either the metal or transparent electrode. After lamination was completed, each device was measured under AM1.5G illumination on a solar simulator to establish the baseline performance, which acts as a reference, for comparison against after stressing has been completed. Each laminate was also photographed to track any visible degradation that might evolve over stressing and external quantum efficiency measurements were made as well.

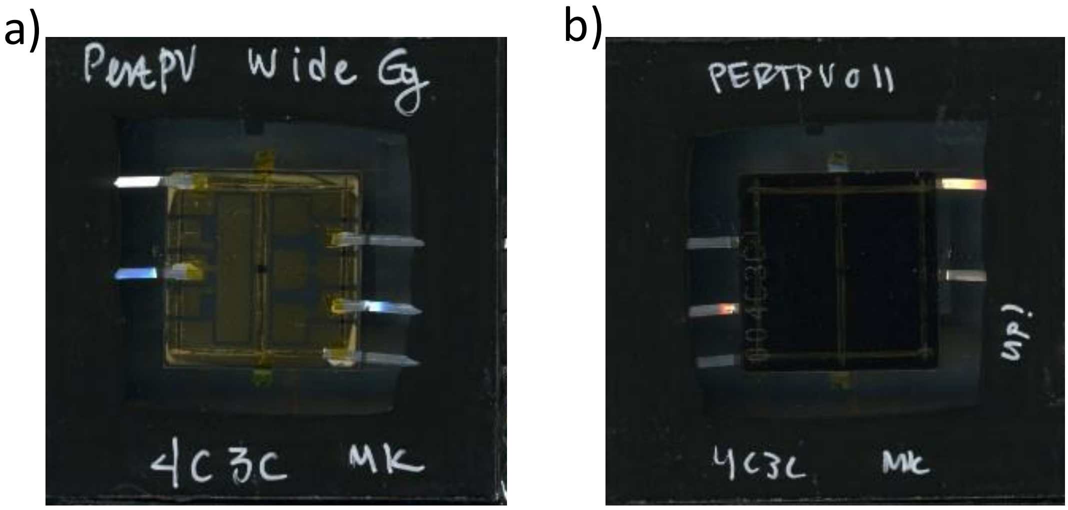

Figure 1. Photographs of a representative UOXF single-junction device after lamination as viewed from the (a) top metal electrodes and (b) the rear transparent electrodes.

4. Single-Junction Solar Cell Stressing Results

The 15 narrow band gap and 15 wide band gap single-junction laminates were randomly split into five separate groups, with each group being loaded into a different environmental stressing chamber to perform one of the five tests indicated in Table 1. The laminates were periodically monitored at intermediate time points during the environmental stressing programmes to gauge their progress and identify if any early failure modes arose.

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4.1 External Quantum Efficiency

The external quantum efficiency spectrum (EQE) was measured for each device at several intermediate time points over the course of the environmental stressing routines. Changes in the EQE spectra can provide useful insight into any failure mechanisms that might arise in the embedded laminate. Additionally, the peak of the EQE derivative can provide a physically relevant measure of perovskite absorber band gap, which can be used to look for any changes that might be occurring in the perovskite material itself. Figure 2 presents an example of the EQE spectra for a wide band gap laminated device at different time points during the damp heat stressing test. Encouragingly, it shows that neither the shape of the EQE spectrum nor its band gap energy (E_g) significantly change over the course of hundreds of hours.

Figure 3 tracks the band gap energy from the EQE derivative peak over time during each of the five environmental stressing tests for both the wide and narrow band gap perovskites. Encouragingly, there is virtually no change from the starting position for all of the devices that have undergone stressing conditions in the dark (*i.e.*, humidity-freeze, thermal cycling, and damp heat). Similarly, very little change in band gap was observed in the UV light soak test at 60°C, with the wide and narrow band gap devices only changing on average by 1 meV and 3 meV, respectively, after receiving a UV dose of 15 kWh/m^2.

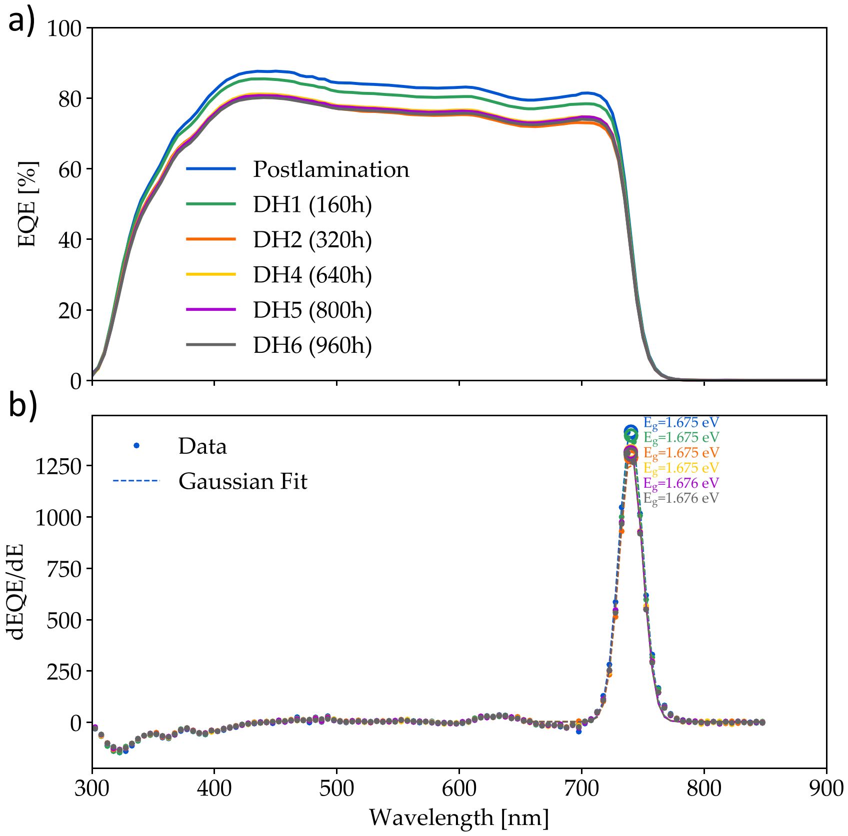

Figure 2. (a) External quantum efficiency (EQE) spectrum and (b) its derivative after different durations in the damp heat stressing programme for a representative wide band gap single-junction perovskite device. The band gap indicated corresponds to the peak of the EQE derivative as determined by a gaussian fit.

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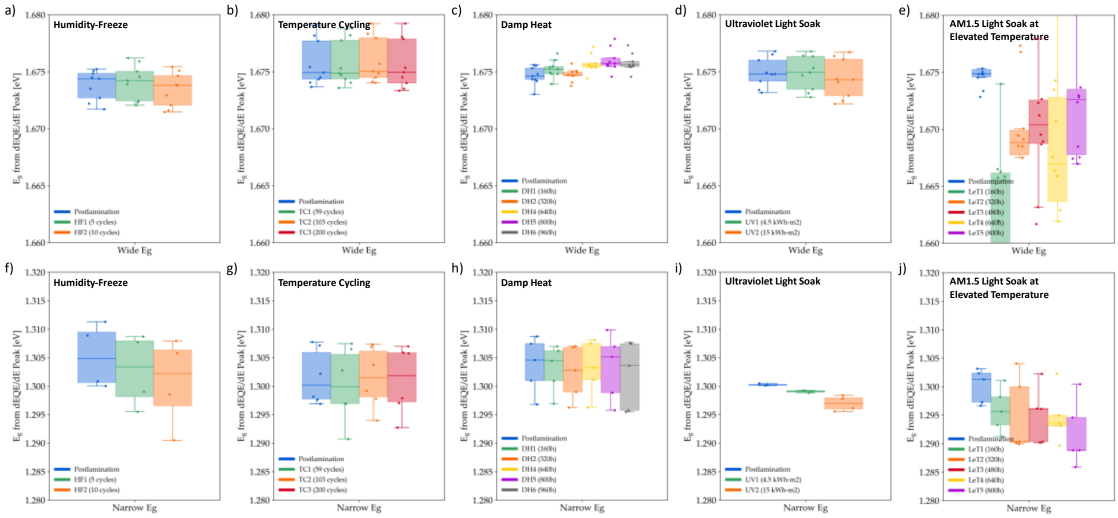

Figure 3. Box plots of band gap energy (E_g) for (a-e) wide band gap and (f-j) narrow band gap single-junction perovskite devices as determined from the derivative of the EQE spectra for each environmental test.

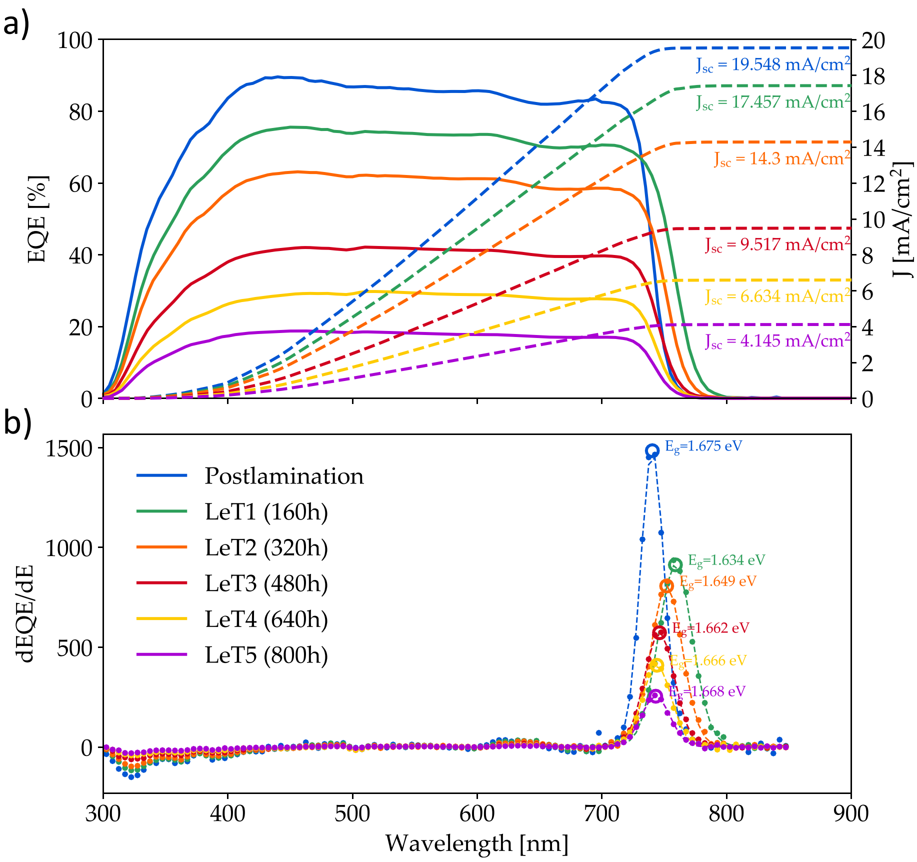

Figure 4. (a) External quantum efficiency spectrum and (b) its derivative after different durations in the light at elevated temperature (AM1.5G spectrum at 60°C) stressing programme for a representative wide band gap single-junction perovskite device. The band gap indicated corresponds to the peak of the EQE derivative as determined by a gaussian fit.

However, more substantial differences were observed in the EQE spectra and band gap energies when the devices were illuminated continually at AM1.5G light stressing and maintained at 60°C. Figure 4 shows that after 160 hours of stressing, the integrated

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current reduced and the band gap notably narrowed by 40 meV. Following each subsequent testing interval, the photocurrent continued to decrease and the band gap gradually blue-shifted back towards its original energy at post-lamination. Since this behaviour was not observed for any of the temperature-based stresses performed in the dark, it is clear that a light-activated process is occurring. This behaviour is not observed in the UV light soak test, but that is likely because the illumination dose is substantially lower. A 15 kWh/m^2 dose of full spectrum sunlight would correspond to only 1.5 h of solar illumination. Therefore, it is likely that the dosage is not high enough in the UV test to observe the process, and indicates that above band gap photon absorption in driving the changes observed, rather than the changes being specifically due to UV light absorption.

4.2 Photovoltaic Performance

Due to the differences observed in the EQE measurements, the photovoltaic performance results presented here are divided into those performed in the dark and those performed under illumination. Note that the power conversion efficiency (PCE) is defined here from the stabilised power measured by maximum power point tracking.

4.1.1 Stressing Tests Performed in the Dark

Figure 5 traces how the power conversion efficiency of each encapsulated solar cell changes from its initial value over the course of stressing in the IEC environmental tests that are performed without illumination. Although these are all thermal tests, the results are quite different between them. Encouragingly, most of the wide band gap and all of the narrow band gap devices pass the temperature cycling test. However, none of the devices technically pass less that 5% degradation requirement for the humidity-freeze test, although one wide band gap perovskite device fails by the smallest of margins, with only 6% loss. Over the course of performing these environmental tests, sometimes devices showed degradation and then later performance recovery. As will be discussed further in Section 4.3, this could be attributed in part to mechanical failure modes such as delamination. It is possible that the degradation yielded by a particular test is reversible and hasn't fully recovered during testing.

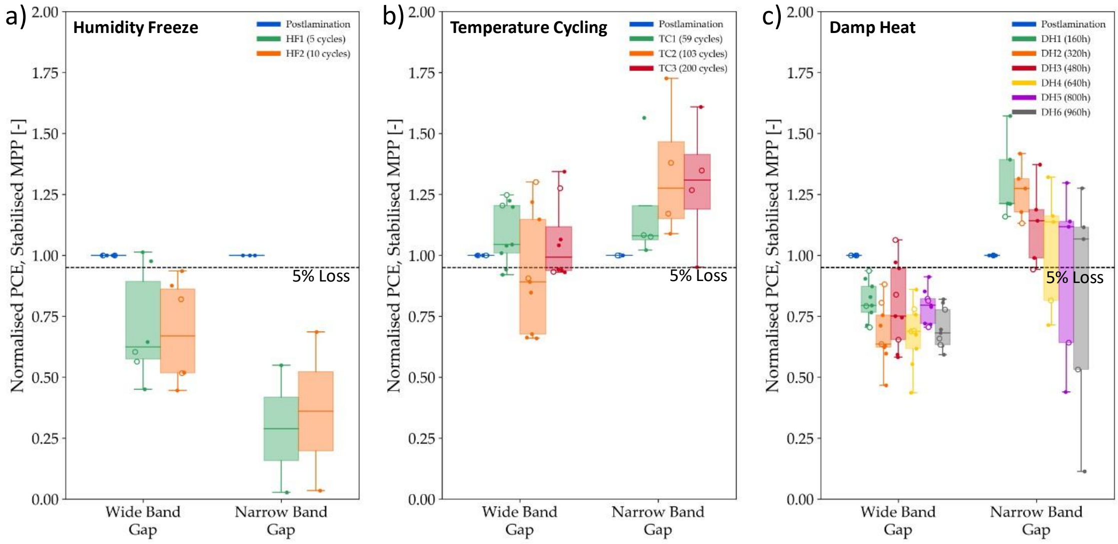

Figure 5. Power conversion efficiency (PCE) of laminated solar cells normalised to its performance after lamination over the course of (a) humidity freeze, (b) thermal cycling, and (c) damp heat environmental stressing tests. The dashed line corresponds to the acceptable power loss of 5% to pass the IEC test. The open circles correspond to 1cm^2 devices and solid circles correspond to 0.25 cm^2 devices.

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4.1.2 Stressing Tests Performed under Illumination

Figure 6 traces how the wide band gap and narrow band gap single-junction laminates performed over the course of stressing at 60°C with either only ultraviolet light or with the full AM1.5G solar spectrum. In contrast to the stress tests that were performed in the dark, significant degradation is observed, with the narrow band gap devices losing nearly all of their performance. The wider band gap material also degrades but at a much slower rate. Because the power losses after 800 hours of stressing under simulated sunlight exceeded 75%, the test was discontinued early.

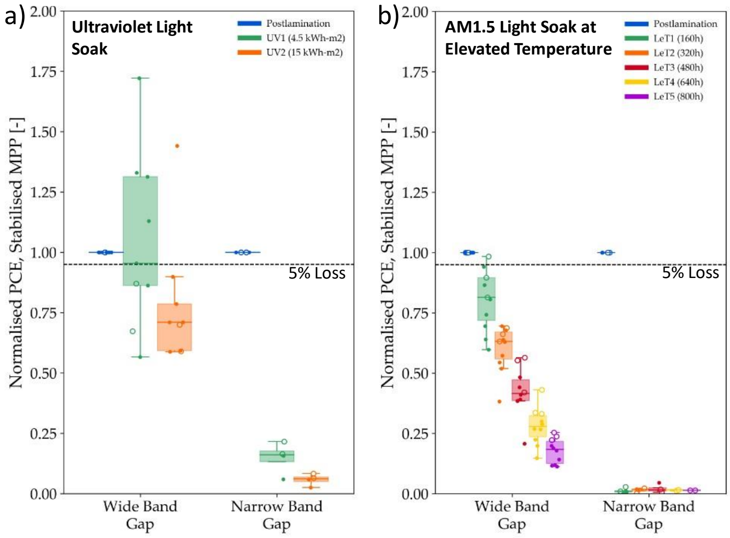

Figure 6. Power conversion efficiency (PCE) of laminated solar cells normalised to its performance after lamination over the course of (a) ultraviolet light soak and (b) AM1.5 light soak at elevated temperature (not an IEC test) stressing tests. The dashed line corresponds to the acceptable power loss of 5% to pass the IEC test. The open circles correspond to 1 cm^2 devices and solid circles correspond to 0.25 cm^2 devices.

Figure 7a shows the evolution of the current-voltage characteristics as measured for a representative wide band gap perovskite device over the course of testing under light at elevated temperature. We observe an initial volage loss of 106 mV and a current loss of 2.6 mA/cm^2 over the first 160 hours of stressing. Thereafter, we confirm the trend observed in the EQE of Figure 4 of continual photocurrent loss with further stressing. The 40 meV narrowing of the band gap could also contribute to some of this initial voltage loss. Notably, the voltage does not recover as the band gap widens with further stressing. In contrast, Figure 7b shows that the narrow band gap device degrades much faster with the photocurrent reaching on average only 0.4 mA/cm^2 within the first 160 hours of stressing.

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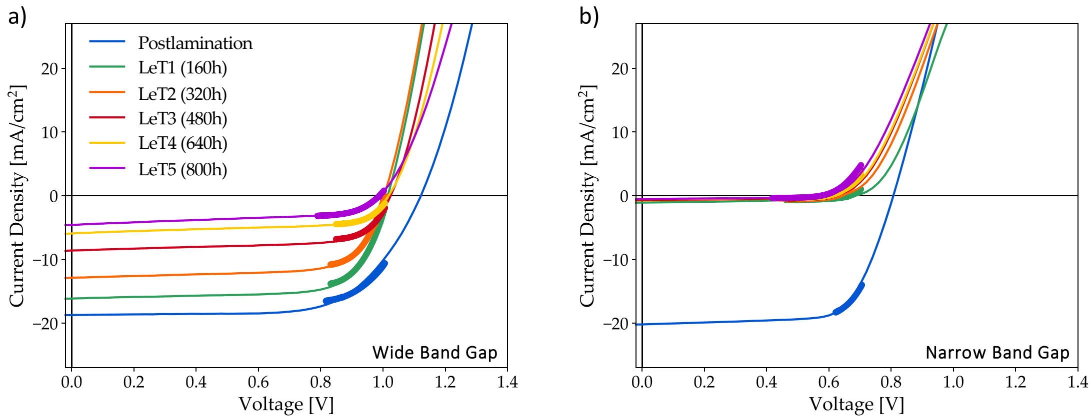

Figure 7. Current-voltage characteristics of maximum power point tracking (dots) and the reverse sweep (line) for a (a) wide band gap and (b) narrow band gap single-junction perovskite laminate over the course of stressing under AM1.5G illumination at 60°C.

4.3 Visual Appearance

The visual appearance of the laminates were also tracked over the course of the environmental stressing because the IEC testing criteria also include a visual inspection. As is shown in Figure 8, over the course of thermal cycling in both the temperature cycling (TC) and humidity-freeze (HF) tests, partial delamination was observed at some of the metal electrodes.

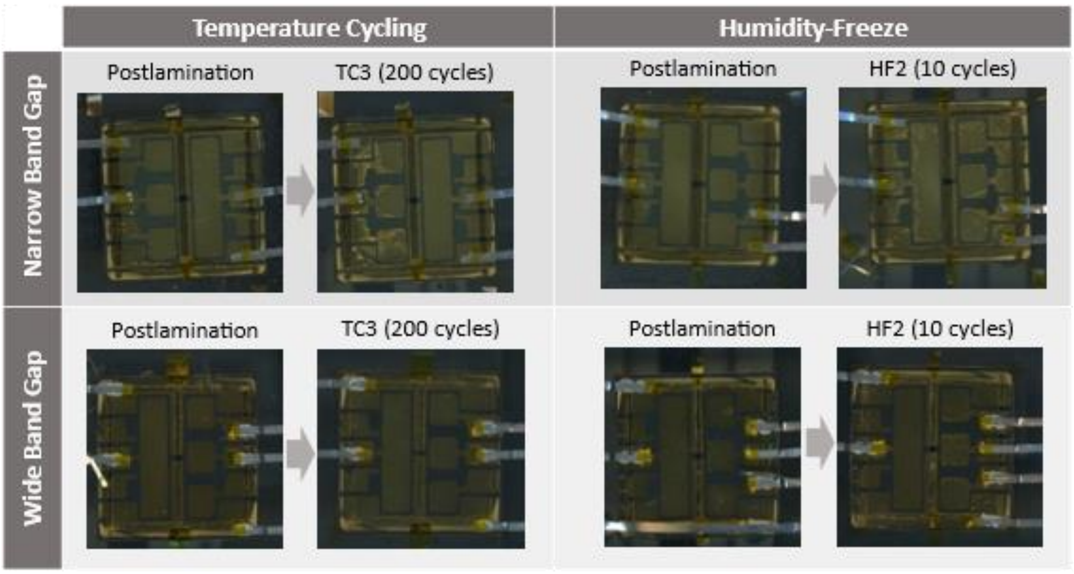

Figure 8. Photographs of wide and narrow band gap devices before and after temperature cycling or humidity-freeze testing show local delamination of some metal electrodes.

Assuming that the regions of delamination do not correspond to material degradation, it is possible that these parts of the electrode could come into or out of contact with the rest of the device stack over the course of the environmental stressing. Intermittent partial electrode contact could account for some of the variability between time points, where degradation and recovery seem to alternate.

Additionally, discoloration occurred over the course of stressing under simulated sunlight at 60°C for several wide band gap devices. Figure 9 identifies that the same features are

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visible from both the top and bottom of the device, which suggests that some reaction is taking place within the full device stack.

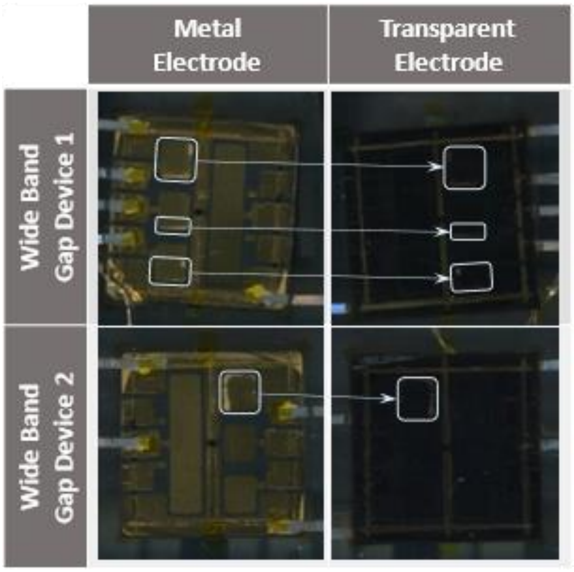

Figure 9. Photographs of two wide band gap devices after 800 hours of AM1.5G illumination at 60°C (LeT5 test point) shows that regions of degradation are visible at both the top and rear contacts of the same device.

5. Discussion

From the body of data collected, it is clear that environmental stressing with perovskite photovoltaic devices is complex on many levels. The observation that some devices improve upon stressing raise the question of whether the devices were originally in a stable state at the start of the stressing programme. Additionally, although the lamination procedure was successful in encapsulating devices, there is likely room for further optimisation. The observation that devices stressed with 85% relative humidity (*i.e.,* humidity-freeze and damp heat) performed more poorly than those tested with temperature cycling suggests that moisture ingress might be occurring into the laminates. This is consistent with the observation that the humidity-freeze test (where the temperature cycling is combined with high humidity) shows accelerated degradation in the air-sensitive narrow band gap devices compared with temperature cycling at ambient humidity alone (see Figure 5).

There are also likely several mechanisms at play within the device stack. Elevated temperature improves the performance of the narrow band gap devices during temperature cycling in the dark, whereas light exposure appears to activate a degradation mechanism in both the wide and narrow band gap perovskites. Visible defects under the metal electrodes suggest that a reaction is taking place somewhere in the device stack. Finally, partial metal delamination shows that mechanical failures are taking place within the device as well during thermal cycling. Altogether, it is difficult to diagnose what the cause is of these observed changes, but it is clear that the behaviour of perovskite devices under environmental stressing is complex and additional failure analysis will be needed to understand the mechanisms before solutions can be engineered.

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Although one of the objectives of the environmental stressing assessment effort was to seek external qualification, this step was not taken in the project for single-junction devices because we were unable to pass the stage gate milestone of achieving less than 5% efficiency losses across all of the in-house testing programmes.

Likewise, in light of the observed degradation modes, particularly those that arise under illumination for the low band gap perovskite material, it was decided to not pursue environmental stressing on two-terminal tandems at this time.

6. Conclusion and Outlook

For this deliverable, we developed lamination procedures that were able to successfully encapsulate perovskite solar cells between two sheets of glass, which allowed them to be subjected to various environmental assessment tests that align with the IEC standards used for industrial PV module qualification. The findings highlight that this effort is complicated and raise questions about whether the devices were originally in a meta-stable state, whether the lamination procedure was optimal, and the nature of the degradation mechanisms at work within the devices. Encouragingly, we observe that the perovskite band gap remains stable for both compositions during all stressing tests that occur in the dark. However, we observe that degradation modes are activated upon the combination of prolonged illumination and heat. At this point, it is unclear at which device layer the instabilities originate and whether there is any interaction between them. The observation of partial delamination of the metal electrodes with thermal cycling indicates that mechanical failures are arising and could be large contributors to decreased performance in tests with temperature cycling. It is encouraging that many devices were able to pass or were close to passing with less than 5% losses in temperature cycling, humidity-freeze, and damp heat. This points to the need for more detailed understanding about the degradation mechanisms that are work so that device stacks can be designed to be mechanically robust and prevent any adverse reactions that might be occurring.

7. References

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