



## Multivariate Approach for Studying the Degradation of Perovskite Solar Cells.

Kettle, Jeffrey; Tyagi, Priyanka; David, Tudur; Stoichkov, Vasil

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1 **Multivariate Approach for Studying the Degradation of Perovskite Solar Cells**

2 **Priyanka Tyagi, Tudur W. David, Vasil D. Stoichkov, Jeff Kettle\***

3 School of Electronic Engineering, Bangor University, Dean St., Bangor, Gwynedd, Wales, UK,

4 \*email; j.kettle@bangor.ac.uk

5

6 **Abstract**

7 Despite the progress in the performance of perovskite solar cells (PSCs), the absorber layer  
8 degradation during prolonged exposure to multiple environmental conditions is still a major  
9 issue. As the degradation depends upon many intrinsic and extrinsic factors, the need to adopt a  
10 multivariate testing protocol, which provides rapid assessment of device stability, is required. To  
11 do this, a Plackett Burman (PB) screening design has been used to analyze 9 different factors that  
12 affect the PSC stability; including four extrinsic factors (oxygen, moisture, UV exposure and  
13 temperature) and five intrinsic factors (selection of hole transport layer and electron transport  
14 layer, absorber layer thickness, halide type and perovskite deposition process). This approach  
15 allows us to rank the relative severity of these factors and can be used to narrow the scope of  
16 materials and device architectures to be modified, by identifying materials and configurations,  
17 which are the most stable. The least and most stable device configurations have been identified  
18 and the success of the screening approach has been demonstrated by testing the optimized  
19 configurations under ISOS-D1 and -L2 protocols. Importantly, only 12 experiments are needed  
20 to establish the most stable combination from the 9 factors thus providing a rapid assessment.  
21 Scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements of perovskite  
22 absorber films have been performed in order to understand the degradation pathways and to  
23 support the conclusion of PB screening technique.

24 **Key words;** perovskite solar cells, stability, multivariate analysis, degradation studies.

25

26

## 27 **Introduction**

28 Perovskite solar cells (PSCs) have attracted attention due to the rapid growth in power  
29 conversion efficiencies (PCEs) over the past decade (Saliba et al., 2016; Li et al., 2016) and the  
30 possibility to integrate them in tandem configuration with traditional silicon solar cells (Sahli et  
31 al., 2018; Kanda et al., 2018). However, the poor stability remains a challenge for their  
32 commercialization. The sources of instability in PSCs are numerous and include intrinsic  
33 properties (perovskite layer composition, hole and electron transporter, electrode etc.) (Boyd et  
34 al., 2019; Christians et al., 2018a; Cao et al., 2018) and external environmental conditions such  
35 as humidity, light, temperature and thermal changes etc. Most studies on PSC stability to date  
36 have been focused on considering one or a maximum of two stress factors e.g. oxygen (O<sub>2</sub>)  
37 (Bryant et al., 2016; Kong et al., 2016) humidity (Song et al., 2016a; Schlipf et al., 2019) or  
38 temperature (Misra et al., 2015). Although the stability study under one applied stress can  
39 provide meaningful information, it does not provide information about the likely outdoor  
40 stability during which multiple stresses are simultaneously applied. This is important for three  
41 reasons; firstly, the outdoor environment is the most likely location for deployment, so PSCs will  
42 experience multiple stresses, which will act simultaneously and vary with time (Christians et al.,  
43 2018b) Secondly, it has been observed that the degradation is accelerated due to the 'interaction'  
44 between stress factors. Thirdly, and surprisingly, it has been shown in PSCs that one stress factor  
45 can also act as the trigger to the degradation from other stresses; an example being that methyl  
46 ammonium lead iodide (MAPbI<sub>3</sub>) absorber layer does not degrade rapidly due to illumination  
47 unless the samples are heated at above 45°C (Misra et al., 2015).

48 Some recent advancement has happened in the degradation studies of PSCs under the combined  
49 stress factors (2 or 3 at a time). Christians et al. have studied the degradation of triple cation  
50 based PSCs (> 1000h) under the effect of three stress factors; light (including UV-light, O<sub>2</sub> and  
51 moisture) (Christians et al., 2018a). Domanski et al have made a very significant contribution in  
52 their study, where they have presented the impact of O<sub>2</sub>, humidity, and temperature on the  
53 operational stability of PSCs. The authors have presented a degradation study of PSCs under one  
54 stress and in the combination of multi-stress factors. They have observed that the PSCs degrade  
55 drastically in the presence of O<sub>2</sub> and humidity (even 5%) and were very unstable at elevated

56 temperature ( $\sim 65^{\circ}\text{C}$ ). Based on their observations, they have also proposed the stable  
57 operational conditions for the PSCs (Domanski et al., 2018).

58 Another very important study on the degradation of  $\text{MAPbI}_3$  absorber layer based PSCs has been  
59 performed by Islam and coworkers where they have performed maximum power point tracking  
60 (MPPT) under continuous light illumination for 4000 h. This study is very important as this is  
61 possibly the longest MPPT till date performed on  $\text{MAPbI}_3$  based PSCs without mixing of cations  
62 in the formulation of perovskite. The studies were performed on encapsulated devices at  $30^{\circ}\text{C}$   
63 without UV filters (Islam et al., 2019).

64         Given the numerous and unknown range of variables that affect PSC stability, a holistic  
65 approach to study stability in PSCs would be beneficial to the community. This would enable  
66 multiple extrinsic and intrinsic factors to be modified simultaneously and their stability assessed  
67 together rather than by ‘one factor at a time’. However, such a ‘multi-stress’ study in conjunction  
68 with device structure variation would be very time-consuming undertaking, particularly if only  
69 one factor was changed for every experiment. Therefore, we propose to use an experimental  
70 screening design from design of experiments (DOE) method, which allows us to undertake  
71 multivariate analysis of the PSC stability. Multivariate analysis techniques such as plackett  
72 burman (PB) have been widely used by the manufacturing and life science industry for process  
73 optimization, demonstrating the validity of this mathematical approach (Waśko et al., 2010;  
74 Alves et al., 2014, Briefs et al., 2013; Jain et al., 2010). Recently, our group has successfully  
75 demonstrated the applicability of PB screening in the performance optimization of field effect  
76 transistors (FETs) with 8 factors in 12 experimental runs (Gomes et al., 2019).

77         It can also be used in the context of PSC reliability by identifying the principle factors  
78 that impact upon stability and aid the design of the PSC to be more stable to extrinsic stress  
79 factors. The approach allows us to 1) rank which intrinsic or extrinsic degradation factor affects  
80 the stability the most and the least and 2) Identify which combination of device  
81 structure/materials yields the most stable device. To complement the statistical analysis, X-Ray  
82 diffraction (XRD) and scanning electron microscopy (SEM) measurements were performed to  
83 understand fully the degradation routes for each stress and change in device structure.

84 In this work, multiple factors were studied by using the PB screening technique, which  
85 can identify the most significant degradation factors using a low number of test runs. The  
86 screening technique is capable of testing factors by requiring only  $n+1$  experiments (Waśko et  
87 al., 2010; Alves et al., 2014; Briefs et al., 2013; Jain et al., 2010). This means a rapid analysis  
88 can be achieved. PB analysis utilizes a predetermined test matrix based upon the number of  
89 factors selected and the matrix used for this test was taken from Esbensen et al (Esbensen et al.,  
90 2018). Four extrinsic stress factors ( $O_2$ , humidity, UV exposure and temperature) and five  
91 intrinsic factors related to device structure (HTL and ETL, absorber layer thickness, absorber  
92 layer composition ( $MAPbI_3$  or  $MAPbBr_2I$ ) and fabrication procedure) were studied for an  
93 ‘inverted’ PSC structure. The PSC device structure is shown in Fig.1. For the study, two levels  
94 for each factor were considered. Based upon the number of factors selected, 12 experiments were  
95 found to be necessary, based upon the PB table.

96

## 97 **2. Experimental details**

### 98 **2.1. Design of experiments and choice of levels/factors**

99 Table 1 and 2 show the detailed range of stress conditions used in each experiment, where ‘L’  
100 indicates the low level and ‘H’ indicates the high level, which can be quantitative or qualitative.  
101 The ‘L’ and the ‘H’ levels, corresponding to each factor, were chosen based upon their impact on  
102 the stability of the PSCs cited in the previous literature. We have selected poly(3,4-  
103 ethylenedioxythiophene)-poly(styrenesulfonate)(PEDOT:PSS) as ‘L’ level for the factor HTL as  
104 it is widely used HTL in inverted PSCs (Xiao et al., 2014; You et al., 2014) and is found very  
105 unstable compared to inorganic HTL due to the hygroscopic nature of this layer (You et al.,  
106 2016). In contrast to PEDOT:PSS, nickel oxide ( $NiO_x$ ) is reported as a very stable HTL in  
107 inverted PSCs (You et al., 2016; Kim et al., 2015; Zhou et al. 2018) which justified the choice of  
108 this material as the ‘H’ level for HTL. For Perovskite absorber layer,  $MAPbI_3$  and  $MAPbBr_2I$   
109 have been chosen as the ‘L’ and ‘H’ levels respectively.  $MAPbI_3$  is very well studied and widely  
110 used absorber layer due to their near complete visible light absorption in the films and efficient  
111 charge extraction due to a high diffusion length for the carriers (Strabks et al., 2013; Lopez et al.,  
112 2017). This absorber layer showed high sensitivity and instability towards moisture and  $O_2$   
113 (Bryant et al., 2016).  $MAPbBr_3$  shows better resistance towards moisture and  $O_2$  due to its

114 crystallographic structure but at a cost of large exciton binding energy and reduced light  
115 absorption, resulting in low PCE in PSCs (Lopez et al., 2017; Edri et al.; 2013). Therefore, we  
116 have selected MAPbBr<sub>2</sub>I as ‘H’ level to compensate for the efficiency and stability (Zhao et al.,  
117 2014). For ETL, with and without lithium fluoride (LiF)/ [6,6]-Phenyl-C71-butyric acid methyl  
118 ester (PC<sub>70</sub>BM) interface were chosen as the ‘H’ and ‘L’ levels because the presence of electron  
119 injection layer improves the stability and reduces hysteresis in PSCs (Wang et al., 2017). LiF  
120 was chosen because it is found to improve the efficiency of the PSCs by the doping of PCBM  
121 (Turak et al., 2017). For the fabrication steps, two-step procedure was considered as ‘H’ level  
122 because it provides a better reproducibility as compare to the one-step procedure (‘L’ level) (Li  
123 et al., 2016; Xiao et al., 2014). Thick films were considered as the ‘L’ level because the devices  
124 consisting thick films were found least efficient due to the increase in recombination resistance  
125 of the absorber layer as compared to the devices with thin absorber layer (~300nm) (‘H’ level)  
126 (Liu et al., 2014).

127 The selection of the extrinsic factors is quantitative. UV exposure degrades the devices faster,  
128 especially in the presence of O<sub>2</sub> (Christians et al., 2018a) so ‘with UV filter’ and ‘without UV  
129 filter’ have been taken as ‘L’ and ‘H’ levels. The ‘L’ (0%) and ‘H’ (20%) levels for O<sub>2</sub>  
130 correspond to the measurements performed in Nitrogen (N<sub>2</sub>) and air. For humidity ‘L’ (< 5%)  
131 and ‘H’ (80%) corresponds to the inert-dry conditions and ambient humidity. The ‘H’ level of  
132 temperature is related to previous literature and the ‘ISOS’ standards which controls temperature  
133 at 65°C during accelerated testing. The ‘L’ level was kept as 45°C, as this is the lower  
134 temperature limit for a solar cell under 1 sun illumination (Koehl et al., 2011; Misra et al., 2015).

135 It is worth noting that the choice of these levels could be different for other set of  
136 experiments, which could lead different resulting conclusions. For the 2-fold PB screening  
137 technique, we are restricted to a choice of only two levels related to each factor. These levels are  
138 summarized in the table below.

139

140

141

142

143 **Table 1:** Plackett-Burman (PB) table used which requires 12 experiments to study the main  
 144 effects of degradation to the perovskite absorber layer.

Run	Extrinsic Factors				Intrinsic Factors				
	O <sub>2</sub>	Humidity	UV	T	Halide	HTL	ETL	Fabrication Step	Thickness
1.	L	L	L	L	L	H	L	H	L
2.	H	H	H	L	H	H	L	H	L
3.	H	H	L	L	H	L	H	L	L
4.	H	L	H	L	L	L	H	H	H
5.	L	H	H	L	L	H	H	L	H
6.	L	L	H	L	H	L	L	L	H
7.	H	L	L	H	L	L	L	L	L
8.	L	H	L	H	H	L	L	H	H
9.	H	L	L	H	H	H	H	H	H
10.	L	H	H	H	L	L	H	H	L
11.	H	H	H	H	L	H	L	L	H
12.	L	L	H	H	H	H	H	L	L

145

146 **Table 2:** Definition of each low ('L') and high ('H') factor defined in table 1.

	O <sub>2</sub>	Humidity	UV	T	Halide	HTL	ETL	Fabrication Step	Thickness
<b>L</b>	0%	< 5%	With UV filter	45°C	MAPbI <sub>3</sub>	PEDOT:PSS	Without LiF	one-step	500nm
<b>H</b>	20%	80%	Without UV filter	65°C	MAPbBr <sub>2</sub> I	NiOx	With LiF	two-step	280nm

147

148

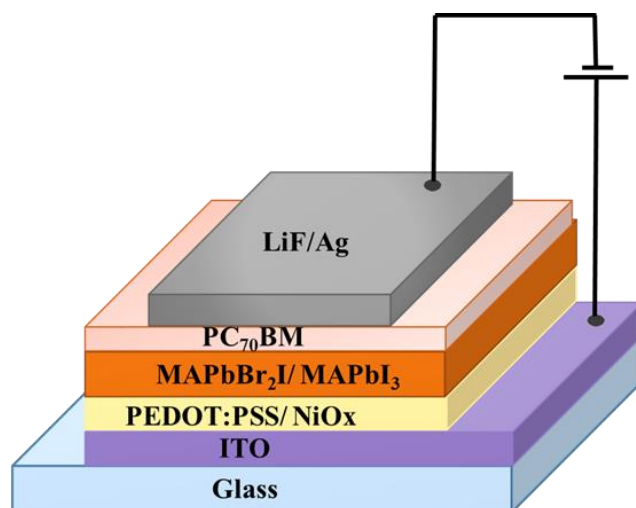
149

150

151

152

153



154 **Fig. 1:** Schematic of Device configuration used for stability studies.

155 A ‘run’ in table 1 is defined as the individual experiment where the device configuration and  
156 stress factors are altered. For clarity, a table has been added to the *SI (Table S1)* explicitly stating  
157 the configuration and conditions used in 12 experimental runs.

## 158 **2.2. Perovskite absorber layers and Device Fabrication**

159 Samples for each run were fabricated on glass substrates, which were cleaned by ultra sonicating  
160 in deionized water, acetone and isopropanol for 20 min each, followed by O<sub>2</sub> plasma treatment  
161 for 5 min. The variation in sample configuration was considered by using two HTLs;  
162 PEDOT:PSS and NiO<sub>x</sub>, two compositions of perovskite (MAPbI<sub>3</sub>, MAPbBr<sub>2</sub>I; each with two  
163 thicknesses), perovskite layer deposition by either one-step or two-step process and including or  
164 excluding the ETL (LiF).

165 Shown in table 2 are the ‘L’ and ‘H’ levels used for this study. PEDOT:PSS (Ossila  
166 Al4083) was spin coated at 4000 rpm for 40 s in ambient conditions and annealed at 150°C for  
167 15 min. NiO<sub>x</sub> solution was prepared by dissolving nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O)  
168 and ethylenediamine in 1:1 molar ratio in ethylene glycol (all from Sigma Aldrich). The solution  
169 was then left for stirring at 70°C for 3 h. NiO<sub>x</sub> films were deposited at 2000rpm for 90 s followed  
170 by annealing at 300°C for 1 h in ambient conditions.

171 For the perovskite layer, three factors were varied; (i) the perovskite composition -  
172 MAPbI<sub>3</sub> or MAPbBr<sub>2</sub>I, (ii) perovskite absorber layer thickness and (iii) the deposition process  
173 (one-step or two-step). The perovskite absorber layers were deposited in a N<sub>2</sub> filled glove box.  
174 For one-step Process, The MAPbI<sub>3</sub> solution was prepared by mixing lead iodide (PbI<sub>2</sub>) and  
175 methylammonium iodide (MAI) in 1:1 M ratio in dimethylformamide (DMF). The solution was  
176 left on stirring for 24 h at room temperature and heated at 70°C for 10 min and during the  
177 deposition. The solution was filtered by using a 0.45 μm PTFE filter. The films were deposited at  
178 2000 rpm and 6000 rpm for 40 sec with an anti-solvent (toluene) treatment in last 10 sec of spin  
179 coating. Samples were annealed at 90°C for 1 h after the deposition. The measured thicknesses of  
180 perovskite layer were approximately 500 nm and 280 nm for 2000 rpm and 6000 rpm films.  
181 MAPbBr<sub>2</sub>I solution was prepared by mixing 433 mg lead bromide (PbBr<sub>2</sub>) and 187.6 mg MAI in  
182 1 ml DMF. The remainder of the solution preparation and film fabrication was kept the same as  
183 for MAPbI<sub>3</sub>. To deposit MAPbI<sub>3</sub> by two-step process, separate solutions of MAI (30 mg/ml) in  
184 isopropanol and PbI<sub>2</sub> (461 mg/ml) in DMF were prepared. PbI<sub>2</sub> solution was spin coated at 2000



185 rpm and 6000 rpm for 40 sec on substrates from a solution heated at 70°C for 10 min. Substrates  
186 were then annealed at 90°C for 20 min. Subsequently, MAI was deposited at 6000 rpm for 40 sec  
187 and films were annealed at 90°C for 20 min. Similarly, for MAPbBr<sub>2</sub>I, the concentration of  
188 solution was 30 mg/ml in isopropanol for MAI and 367 mg/ml in DMF for PbBr<sub>2</sub>. The spin  
189 coating procedure was similar to that of the MAPbI<sub>3</sub>. Both the PbI<sub>2</sub> and PbBr<sub>2</sub> solutions were  
190 filtered using a 0.45 µm PTFE filter.

191 After perovskite layer deposition PC<sub>70</sub>BM was deposited at 4000 rpm for 40 sec from a  
192 solution of 30 mg/ml PC<sub>70</sub>BM in Chlorobenzene (CB). Finally, a layer of LiF was thermally  
193 evaporated at a pressure of 1x10<sup>-6</sup> torr if required. To fabricate the inverted PSCs, Indium Tin  
194 Oxide (ITO) coated glass substrate was used. The rest of the fabrication procedure was the same  
195 as mentioned above and at the top silver (Ag) electrode was deposited at a pressure of 1x10<sup>-6</sup>  
196 torr. The active area of the devices was 1cm<sup>2</sup>.

197

### 198 **2.3. Absorption Measurements and Device Characterization**

199 After fabrication, all samples were transferred to a UHV environmental chamber with controlled  
200 temperature and environment and optical feedthroughs. Depending on the test run, the samples  
201 were exposed to either a N<sub>2</sub> atmosphere (99.9%) or dry air (80% N<sub>2</sub>, 20% O<sub>2</sub>) and relative  
202 humidity was adjusted by injecting water vapor via a feed through and controlled in-situ with a  
203 calibrated sensor (lower limit is 5%) used to maintain the relative humidity. Samples were placed  
204 onto a heated stage with sample temperature measured using a thermocouple. In all experimental  
205 runs two samples were tested under sulphur plasma class AAA lamp (Plasma-I systems GmbH)  
206 at AM 1.5. For absorption studies, transmission mode measurements were conducted by using an  
207 optical fiber of 400 µm core integrated with ocean optics spectrometer model HR4000. For  
208 device studies, BNC feed through allowed the samples to be connected to an external Keithley  
209 SMU. In this work, the time taken to reach 80% (T80%) of the original value (absorption of  
210 perovskite absorber layer ) or 50% of the final value (T50%) were calculated and were used as  
211 the ‘output responses’ for each test run. To aid the analysis, a software package (Reliasoft) was  
212 used for multivariate analysis. XRD measurements were performed using a Philips X-PERT  
213 3040/60 instrument at 40kV voltage and 30mA current with CuK $\alpha$  radiation. SEM measurements  
214 have been performed using Hitachi TM3000-table top SEM.

215 **3. Results and Discussion**

216 To analyze how changing the factors affect stability, the time taken for the samples to reach two  
 217 particular lifetime points has been measured; T80% (defined as the time to reach 80% of the  
 218 initial value) and T50% (for 50% of initial value). A life test model was developed that uses a  
 219 least square polynomial model to express the effects in terms of the stress factors or  
 220 environmental conditions. Least square mean values were calculated by assuming this model of  
 221 the characteristic life time as shown in eq. 1.

222 
$$y_i = f_0 + \sum_{k=1}^z f_k x_{nk} + \varepsilon_n \quad (1)$$

223 Where  $y_i$  represents the response,  $f_0$  is a constant fitted parameter,  $f_1$  to  $f_k$  are the fitting  
 224 parameters for the individual coefficients,  $x_{nk}$  represents the  $n^{\text{th}}$  level of the  $k^{\text{th}}$  predictor variable  
 225 and  $\varepsilon_n$  represents the standard variance error. Multiple ‘y’ observations (representing the T80%  
 226 or T50% time) can be expressed with the matrix in eq. 2.

227 
$$y = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix} X = \begin{bmatrix} 1 & x_{11} & x_{12} & \cdot & x_{1n} \\ 1 & x_{21} & x_{22} & \cdot & x_{2n} \\ \vdots & \vdots & \cdot & \cdot & \cdot \\ 1 & x_{n1} & x_{n2} & \cdot & x_{nn} \end{bmatrix} \quad (2)$$

228 The matrix X is denoted as design matrix containing information about the level of the predictor  
 229 variable. The main effect of the experimental factors can be solved using eq. 3 (Esbensen et al.,  
 230 2018)

231 
$$E_X = 2[\sum(y+) - \sum(y-)]/N \quad (3)$$

232 where  $y+$  represents the high-level term,  $y-$  represents the low-level terms and  $N$  represents the  
 233 total number of experiments. The main effects are assumed to have the same variance, defined as  
 234  $\sigma^2$ , given in eq. 4. Here  $E_X$  represents the factors and  $\mu$  is the calculated mean.

235 
$$\sigma^2 = \frac{\sum(E_X - \mu)^2}{N-1} \quad (4)$$

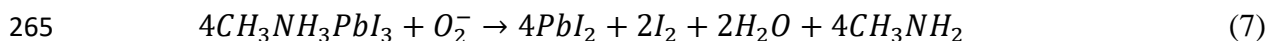
236 In order to identify a regression line, the standard error must be accounted. The standard error of  
 237 the estimate is a measure of the accuracy of predictions and given in eq. 5.

$$\sigma_{est} = \sqrt{\frac{\sum(Y_{real}-Y_{est})^2}{N}} \quad (5)$$

Where  $\sigma_{est}$  is the standard error of the estimate,  $Y_{real}$  is an actual value and  $Y_{est}$  is an estimated value. The numerator is the sum of squared differences between the actual scores and the predicted scores. The mean squared error is  $F_{MS}$  dependent on the mean squared factor, which is related to the variance of single quantity as shown in eq. 6.

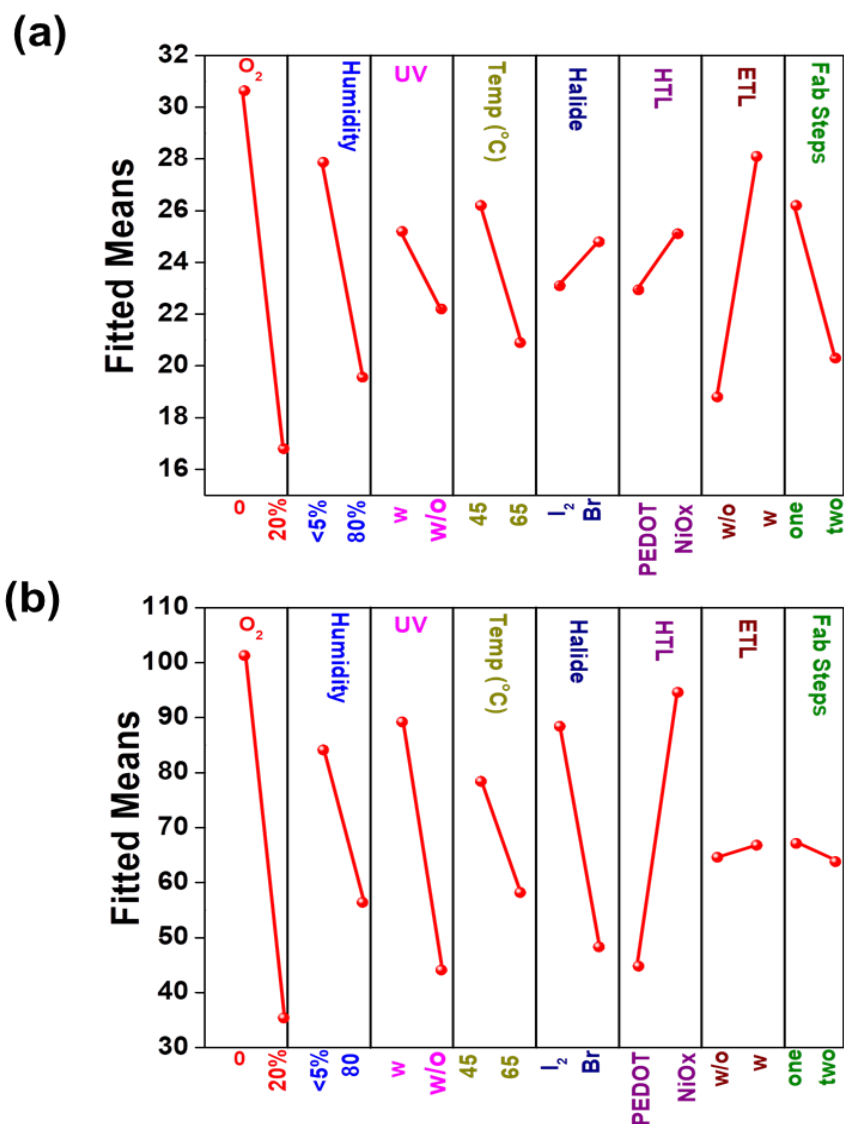
$$F_{ms} = \frac{(E_X)^2}{N} \quad (6)$$

Fitted mean values are obtained from the multivariate analysis for ‘H’ and ‘L’ values of each factor. Figure 2 illustrates the variation of the fitted means for ‘L’ and ‘H’ levels of each factor (predictors) calculated from multivariate analysis. To calculate the fitted means, least square regression analysis has been applied to calculate the mean response values within a factorial design (2-fold PB design in our case). Fitted means can be used to identify the variation in the responses (T80% and T50% in this case) due to the change in the level of a particular factor (i.e. ‘L’ to ‘H’ and vice versa). A systematic procedure to obtain Fig. 2 is given in *SI (section S2)*. A higher value of fitted means for a particular level/factor is desirable as this will lead to a higher T80% or T50% time. However, the difference between the fitted means of the ‘L’ and ‘H’ level in a particular factor shows how influential this factor is in affecting the overall stability; a larger difference shows this factor has a greater impact on stability. The multivariate analysis has enabled us to determine the significance of all the stress factors. The difference between the larger and smaller value of fitted mean (FM) was calculated and plotted as a function of stress factor in the order of significance in Fig. 3(a) for T80% and 3(b) for T50%. From the data in Fig. 2, it is clear that for T80% and T50% responses, the presence of O<sub>2</sub> has the most significant impact on the stability of the PSC, which is evidenced by the greatest difference between the fitted means of the ‘L’ and ‘H’ level. The exposure of the absorber layer to O<sub>2</sub> and light leads to the formation of superoxide (O<sub>2</sub><sup>-</sup>) species, which react with the organic cation (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>) of the photoexcited absorber layer. This mechanism is one of the root causes of degradation in the presence of O<sub>2</sub> (Boyd et al., 2019 ; Bryant et al., 2016).



266 It has also been observed that the oxygen can diffuse into the solar cell structure and can  
 267 become a more severe factor in the device instability.

268



**Fig. 2: Term effect plots of two-level Plackett-Burman design completed using perovskite absorber layers. The results show perovskite’s susceptibility to all explored main factors up to (a) T80% and (b) T50%.**

269 The next (second) most significant factor affecting the stability depends on whether one is  
 270 studying the degradation to T80% or T50%. In the case of T80%, the second most significant

271 factor was found to be the ETL. In this study, an inverted structure has been used, where the ETL  
272 is the topmost layer. The ETL can restrict the ingress of O<sub>2</sub> and moisture depending upon its  
273 morphology (Lin et al., 2018). However, PCBM is a hydrophobic layer its alone use cannot  
274 restrict the ingress of O<sub>2</sub> and moisture through the PSC structure. It can act as a barrier for these  
275 extrinsic factors by reducing gas permeation through it by the *n*-type doping (Wang et al., 2017).  
276 As it is the topmost layer, it is likely to be affected by degradation first, then after the ‘barrier’  
277 layer is degraded; it has a lesser and lesser impact as time progresses (which is why it does not  
278 feature so prominently in the T50% data in Fig. 3).

279 The third most important factor to impact upon T80% degradation time was found to be  
280 the presence of humidity. It is known that perovskite absorber layer reacts with water and forms  
281 CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>-H<sub>2</sub>O compound, which then dissociates into CH<sub>3</sub>NH<sub>3</sub>I and (Song et al., 2016a;  
282 Schlipf et al., 2019). This consequently leads to the degradation of perovskite absorber layer.

283 The next most significant factor appeared to be whether a two-step process was adopted  
284 for absorber fabrication over a one-step process. This can be explained by considering the two-  
285 step process of perovskite formation, which relies on the inter-diffusion of MAI into PbI<sub>2</sub>.  
286 However, this process is reported as a reproducible procedure, still this leaves the possibility of  
287 unreacted PbI<sub>2</sub> in the perovskite, which was found to be the case in the present study by XRD  
288 measurements (see *SI Fig. S5*).

289 The difference in fitted means becomes smaller for the remaining factors, so it becomes  
290 more challenging to ‘rank’ relative severity of subsequent factors. However, it can be deduced  
291 that reducing the temperature and filtering the UV light can improve the stability. This is to be  
292 expected, as at elevated temperatures, MAPbI<sub>3</sub> dissociates into PbI<sub>2</sub>, which is the main cause of  
293 degradation. In addition, UV radiation leads to the excitation of electrons in the absorber layer.  
294 These photo-excited electrons react with O<sub>2</sub> to form O<sub>2</sub><sup>-</sup> and leads to the degradation of  
295 perovskite absorber layer. Finally, the data shows that to achieve higher stability, replacing  
296 iodide ions with bromide ions in the absorber layer and by adopting NiO<sub>x</sub> as the HTL leads to  
297 greater stability, when considering the time taken to reach T80%.

298 In case of T50%, the general trend for enhancing the stability has changed as compared to  
299 T80% degradation. Now the order of significance of the factors affecting stability is O<sub>2</sub>, HTL,

300 UV, halide type. O<sub>2</sub> is still the most significant factor that affects degradation to T50%.  
301 However, the selection of HTL and the filtering of UV light are now the second and third most  
302 significant factors. The impact of HTL on T50% is significantly larger in comparison to that on  
303 T80%.

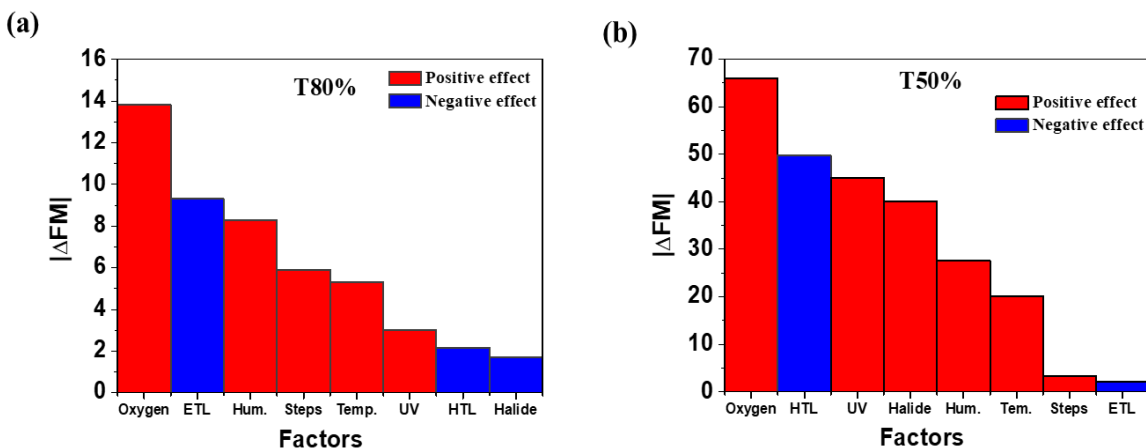
304 This is because the HTL can only interact with O<sub>2</sub> and moisture after their diffusion  
305 through the PSC structure (ETL, thick absorber layer). The HTL contributes less in initial  
306 degradation as a thick absorber layer protects it against these extrinsic factors (Boyd et al., 2019).  
307 However, the lateral diffusion of these species also takes place and does still have a minor role in  
308 the initial degradation of HTL. Among the HTLs used in this study, PEDOT: PSS has a high  
309 absorptivity of moisture, as it is water-soluble. However, under continuous illumination, its  
310 reactivity with moisture decreases due to the increase in temperature. Furthermore, PEDOT: PSS  
311 degrades itself with time and undergoes a phase separation (PEDOT rich and PSS rich phases),  
312 consequently the PEDOT rich phase becomes more susceptible towards O<sub>2</sub>-induced degradation  
313 (Norman et al., 2010). This might be contributing in still making O<sub>2</sub> a prominent factor in T50%  
314 degradation. The next significant factors in the order of decreasing significance were halide  
315 variation, humidity and temperature. Perovskite absorber layer in itself undergoes several  
316 changes under continuous illumination including halide segregation, ion migration, and the  
317 compositional degradation. These chemical changes become rapid in the presence of other  
318 external factors like O<sub>2</sub> and moisture (Boyd et al., 2019; Song et al., 2016b) and become more  
319 severe with prolonged exposure. This indicates that the composition of perovskite absorber layer  
320 plays a more significant role in further 30% degradation than the initial degradation.

321 It has been observed from Fig. 3 that the order of significance of factors affecting the  
322 degradation to T80% and to T50% was different. It has been explained in the previous section  
323 how some factors such as O<sub>2</sub>, the morphology of ETL and humidity can affect the initial  
324 degradation and at a later stage, the decomposition of the absorber layer and internal degradation  
325 of HTL can dominate the process. In the case of PSCs, there are some reports where different  
326 states of degradation have been observed; initial fast degradation ('burn-in') and later slow or an  
327 almost linear regime of degradation (Domanski et al., 2018; Domanski et al., 2017; Abate et al.,  
328 2015). The degradation states were found dependent on different factors (intrinsic and extrinsic).  
329 However, it has been observed that prolonged exposure of PSCs can cause severe degradation

330 mainly due to the degradation of organic materials, perovskite absorber layer/transport layer  
 331 interfaces and contact degradation.

332 Similar observations have been made in silicon PVs, where the dominant failure modes in  
 333 PV changes depending on the time it has been outdoors (or more specifically the current state of  
 334 degradation) i.e. solder contacts tend to fail early in the life cycle, ethylene-vinyl acetate (EVA)  
 335 discolouring occurs later. The discolouring is due to the bleaching oxygen and is a consequence  
 336 of prolonged exposure of EVA to UV radiation and temperature. This can also occur due to the  
 337 poor crosslinking and additives in the EVA formulation (Kuitche et al., 2014). We think this  
 338 work shows that PSCs have similar characteristics because we see that different factors have  
 339 greater or lesser affect depending on if the time is T80% or T50%.

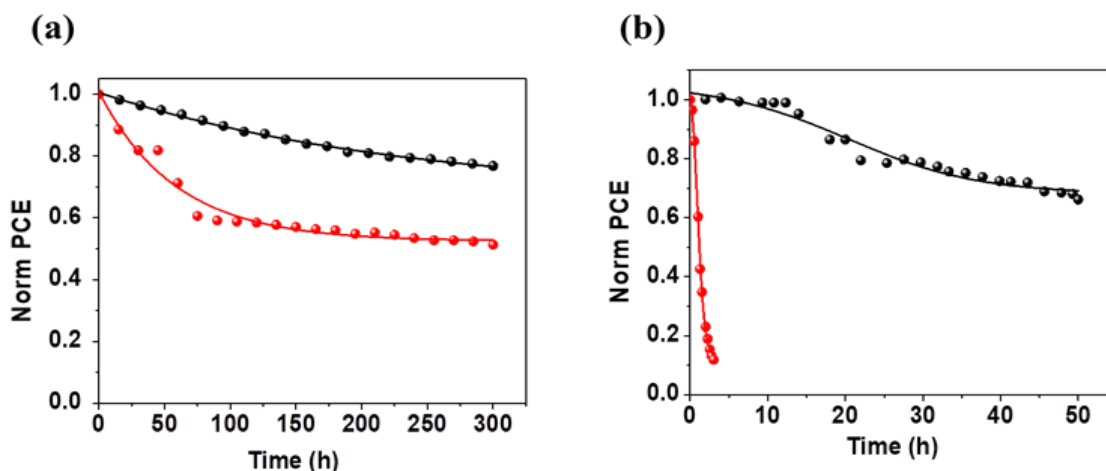
340



**Fig. 3: The absolute difference between the highest and lowest fitted means ( $|\Delta FM|$ ) showing the significance of factors for (a) T80% and (b) T50% values. A positive effect indicates that the ‘L’ level is preferred for higher stability.**

341 To verify the studies, the most and least stable combinations were identified from PB screening  
 342 and compared for stability. The most stable structure was NiO<sub>x</sub>/MAPbBr<sub>2</sub>I/PC<sub>70</sub>BM/LiF/Ag  
 343 (Device ‘A’) and the least was PEDOT:PSS/MAPbI<sub>3</sub>/PC<sub>70</sub>BM/Ag (Device ‘B’). PSCs with these  
 344 structures were fabricated. The PCE for Device ‘A’ was 5.0% and for Device ‘B’ was 8.2% with  
 345 an active area of 1cm<sup>2</sup>. The efficiency for Device ‘A’ is comparable to that reported with  
 346 MAPbBr<sub>2</sub>I as an absorber layer (Zhao et al., 2014). The variation of photovoltaic parameters for  
 347 these devices has been shown in *SI (Fig. S4)* averaged from 5 devices. The variation of PCE as a

348 function of time is shown in Fig. 4(a) (in accordance with ISOS-D-1) and light soaking Fig. 4(b)  
 349 (in accordance with ISOS-L-2). Device ‘A’ shows a T80% of 255 hours during ISOS-D-1 testing  
 350 and 32 hours during ISOS-L-2 testing, whereas Device ‘B’ shows T80% of 35 hours and 3 hours  
 351 for the same respective tests. It is clear from both sets of experiments that Device ‘A’ shows  
 352 greater stability, confirming that this multivariate analysis approach can be used to identify the  
 353 best combination of materials to enhance device stability.



**Fig. 4: Normalized power conversion efficiency as a function of time for Device ‘A’ (black symbol and line) and Device ‘B’ (red symbol and line) solar cell measured by (a) ISOS D-1 (stored in the dark and ambient temperature) (b) ISOS-L2 (under continuous light exposure with controlled 65°C temperature).**

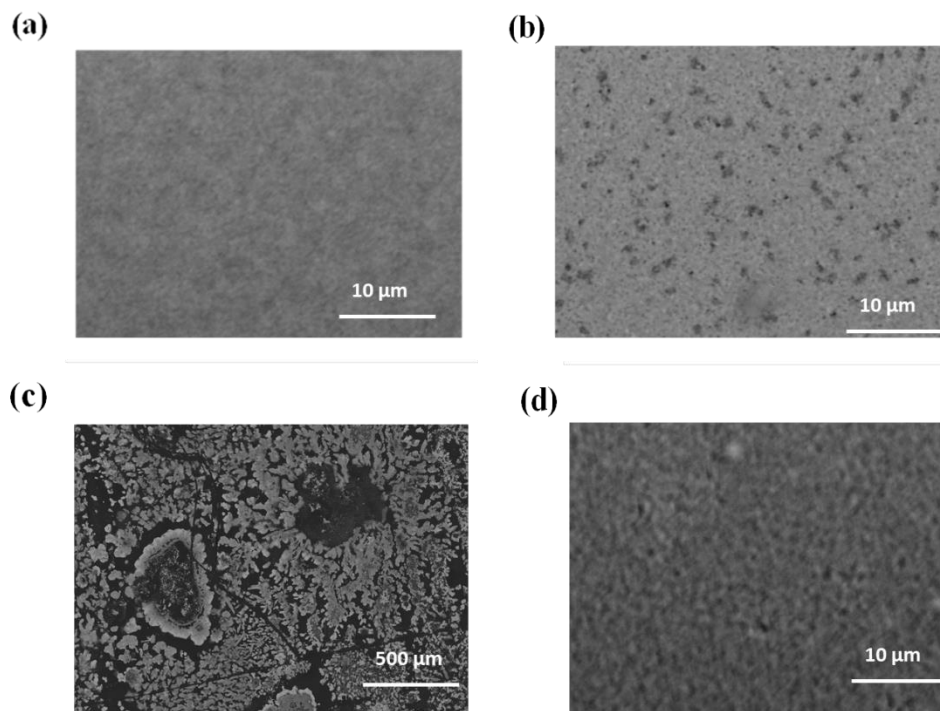
354 Additional material analysis was conducted in order to investigate the degradation mechanisms.  
 355 XRD and SEM measurements can be effectively used to analyze the samples upon degradation  
 356 and identify the mechanism of this degradation. Here, SEM and XRD measurements were  
 357 performed on the fresh and degraded films for all test runs. First, the analysis for fresh samples  
 358 was performed to investigate the effect of device structure. One-step with anti-solvent treatment  
 359 processed films showed no pin-holes while the two-step processed film showed small size pin-  
 360 holes with low density (*SI Fig. S5*). MAPbI<sub>3</sub> fabricated by two-step process showed an unreacted  
 361 PbI<sub>2</sub> peak in the XRD measurements. Further, the NiO<sub>x</sub> supported better formation of perovskite  
 362 film in comparison to PEDOT:PSS, which was observed by SEM and XRD measurements (*SI*  
 363 *Fig. S6*). The effect of perovskite layer thickness was found more prominent on MAPbBr<sub>2</sub>I films  
 364 (*SI Fig. S7*).



365 The PB approach can also be used to deduce some of these effects of degrading the  
366 samples by material analysis studies. This is somewhat difficult to do as the approach is  
367 primarily for studying multivariable using minimal test runs to acquire data quickly and not for  
368 detailed material studies. However, some trends can be observed to aid the understanding of  
369 degradation pathways.

370 Figure 5 shows the SEM images of fresh and degraded samples from Run 1 (as defined in  
371 Table 1). The fresh sample (Fig. 5(a)) did not show any film deformation or pinholes. The  
372 degradation of the film under continuous light illumination without any additional stress factors  
373 is shown in Fig. 5(b), where pin-holes of about 1 $\mu$ m size can be observed in the samples. Fig.  
374 5(c) shows the film degraded under continuous light illumination with humidity and O<sub>2</sub> (sample  
375 from run 11) and 5(d) with UV exposure (sample from run 12). The presence of UV light has  
376 caused the formation of small size pinholes with a larger density, but the humidity and O<sub>2</sub> affects  
377 the films more drastically leading to very large size deformities.

378 The results are consistent with other reports; the exposure to humidity and O<sub>2</sub> leads to  
379 decomposition of perovskite into its constituent materials (Song et al., 2016b). MAPbI<sub>3</sub>  
380 decomposes into MAI and PbI<sub>2</sub>, which can further decompose into Pb and iodine (Juarez-Perez  
381 et al., 2018). This would account for the large sized pinholes observed in SEM images. The  
382 effect of light and UV can be explained by the reaction of photo excited electrons in perovskite  
383 with O<sub>2</sub> which form O<sub>2</sub><sup>-</sup>. This O<sub>2</sub><sup>-</sup> reacts with the organic part of the perovskite layer, which leads  
384 to decomposition of perovskite absorber layer. However, the results highlight the relative  
385 severity and show how the presence of two or more stress factors can significantly accelerate the  
386 process of degradation of perovskite absorber layer. Although the optical and morphological  
387 analysis cannot guarantee a certain pattern in device degradation but it can assure valid stable  
388 operational conditions.

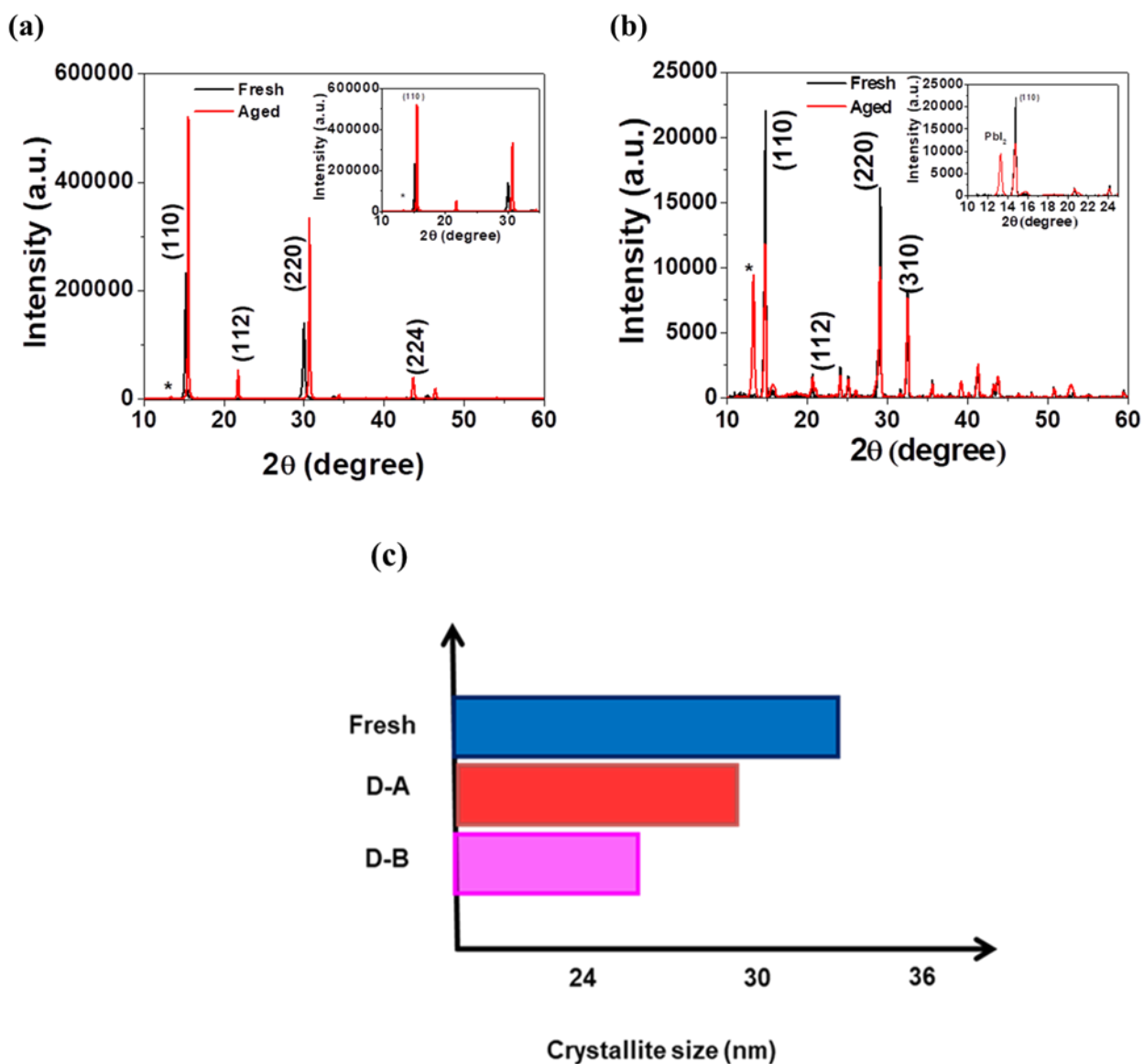


**Fig. 5: SEM image of (a) fresh sample (run 1), (b) sample degraded under continuous light exposure without any extrinsic stress (sample from run 1) and (c) with humidity and O<sub>2</sub> (sample from run 11) (d) with UV (sample from run 12).**

389 XRD measurements were used to study the differences in degradation between MAPbBr<sub>2</sub>I and  
390 MAPbI<sub>3</sub> samples tested during the PB screening tests. Figure 6 shows the XRD spectra of fresh  
391 and degraded (a) MAPbBr<sub>2</sub>I and (b) MAPbI<sub>3</sub> samples. In case of MAPbBr<sub>2</sub>I, peaks  
392 corresponding to several crystalline structures were observed in the fresh sample and are  
393 highlighted in the Fig 6(a). All the crystalline peaks shifted to higher angles in the degraded  
394 samples. This may be attributed to the slight decrease in d-spacing or phase change in perovskite  
395 due to degradation. On the other hand, the effect of degradation on MAPbI<sub>3</sub> is different. There is  
396 no major shift in the crystalline peaks; however, an additional peak of PbI<sub>2</sub> appeared (Fig. 6(b)).

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**Fig. 6:** XRD spectrum of fresh and degraded (under humidity and O<sub>2</sub>) (a) MAPbBr<sub>2</sub>I, sample from run 2 (b) MAPbI<sub>3</sub>, sample from run 11. Significant XRD peaks are marked in the figure (c) Crystallite size calculated from the XRD spectrum for fresh and degraded sample MAPbI<sub>3</sub>. D-A: degraded sample under humidity and O<sub>2</sub> and D-B: degraded sample under heat and UV.

399 Degradation can be quantified by crystallite size variation. The crystallite size was found to be  
 400 60±3 nm in case of fresh MAPbBr<sub>2</sub>I sample. We have observed a shift in (110) crystalline peak  
 401 of diffraction towards the higher angle. This may be attributed to loss of iodide or phase change  
 402 in perovskite due to degradation (Cui et al., 2016). Indeed, perovskite swelling of more than 50  
 403 times (in the thickness) by aqueous solutions have been observed by Song et al. (Song et al.,

404 2015). The variation of crystallite is shown in Fig. 6(c) for MAPbI<sub>3</sub>. The crystallite size was  
405 found to be 34 nm in fresh MAPbI<sub>3</sub> sample reduces to 29 nm in case sample exposed to O<sub>2</sub> and  
406 humidity and 25nm in case sample exposed to UV and temperature. This reduction in crystallite  
407 size is attributed to the change in morphological changes in the perovskite films under different  
408 stresses. As we have discussed earlier, MAPbI<sub>3</sub> decomposes into MAI and PbI<sub>2</sub>, which can also  
409 decompose into Pb and iodine under O<sub>2</sub> and humidity. The perovskite layer also suffers from  
410 photo oxidation and phase change under UV and temperature. We have calculated the crystallite  
411 size of PbI<sub>2</sub> formed under these stresses. The crystallite size of PbI<sub>2</sub> was found to be 31 nm under  
412 humidity and O<sub>2</sub> stress and 12 nm under UV and 65°C. This may be a result of the difference in  
413 the rate of decomposition of MAPbI<sub>3</sub> into PbI<sub>2</sub> under both the conditions.

414 These results support the PB screening conclusions where we have observed that the  
415 presence of O<sub>2</sub> and humidity has severe impact on PSC stability, within this testing range.

#### 416 **4. Conclusions**

417 A two-fold multifactorial analysis based on Plackett -Burman screening technique has been used  
418 to screen the most and least significant factors in the degradation of PSCs. In total 9 factors have  
419 been studied under 12 test runs; four extrinsic (O<sub>2</sub>, humidity, temperature and UV exposure) and  
420 five intrinsic (transport layers, halide type, absorber layer thickness and perovskite deposition  
421 process). To our knowledge, this is one of the most comprehensive stability studies undertaken  
422 on PSCs in terms of factors studied. The data obtained has been analyzed by multivariate  
423 analysis and the fitted means corresponding to the high and low values of each stress factor have  
424 been used to deduce the most and least significant factors. This analysis enables us to select the  
425 materials and device configuration to get the most stable PSC structure. We have fabricated  
426 the most stable and least stable PSC devices based on the conclusion made by PB screening and  
427 tested their reliability under ISOS-D1 and ISOS-L2 protocols. The time related to T80%  
428 degradation of most stable device was measured to be 255 hours and 32 hours under ISOS-D1  
429 and ISOS-L2 protocols. SEM and XRD measurements have been performed to find the  
430 compressive details about the morphological and structural change in perovskite layer while  
431 subjected to different stress factors for all 12 runs.

432

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435 (SPARC II) project, gratefully funded by WEFO.

436 **Supporting Information**

437 Specification of experimental runs used and time dependent absorption measurements, Time  
438 dependent absorption measurements and calculation of fitted means; absorption spectrum of  
439 perovskite absorber layers, decay curve for 12 experimental runs, calculated T80% and T50%  
440 values for each experimental run; Device performance; SEM and XRD measurements of freshly  
441 prepared and aged samples.

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