Supporting Information

X-ray induced modification of the photophysical properties of $MAPbBr_3$ single crystals

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SPS spectra in the below-gap region

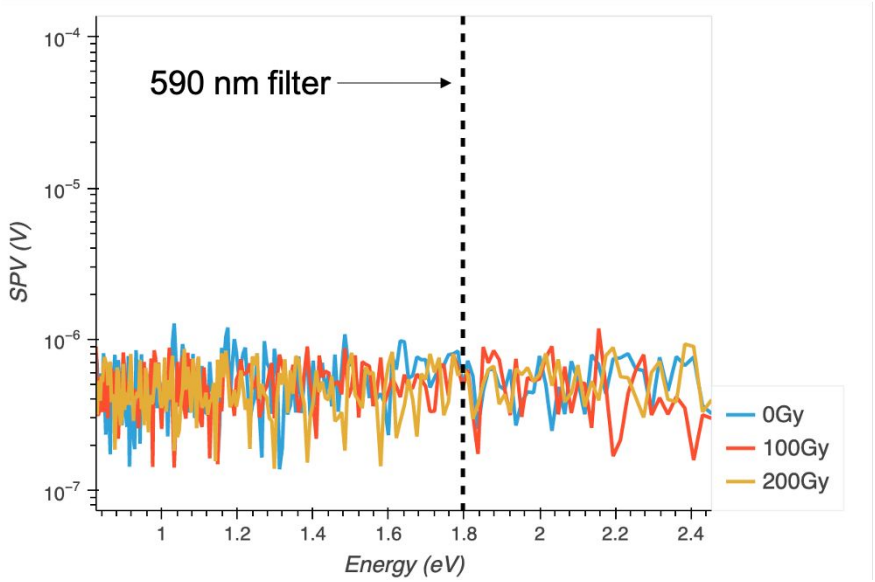

Figure S1: SPS spectra in the below-gap region acquired on a pristine sample (light blue curve) and after 100 Gy (red curve), and 200 Gy (yellow curve) irradiation. The vertical dashed line indicates the cutoff wavelength of the 590 nm long-pass filter. Within the sensitivity of the setup, no deep states were detected after irradiation.

High resolution X-ray diffraction (HR-XRD) on $MAPbBr_3$ single crystal before and after X-ray irradiation

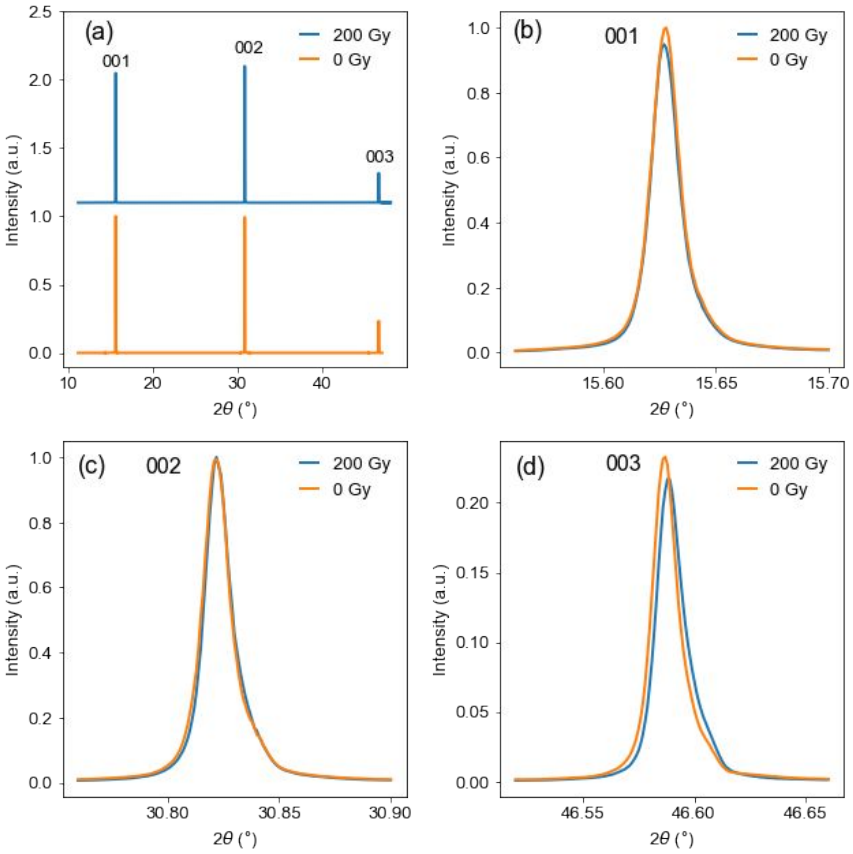

Figure S2: (a) High resolution X-ray diffraction spectrum of a $MAPbBr_3$ single crystal before (orange curve) and after (blue curve) 200 Gy irradiation by W target X-ray tube. Detail of 001 (b), 002 (c) and 003 (d) diffraction peaks.

Description and results of the XPS calibration experiment

In this experiment we acquired 5 consecutive XPS spectra (duration 1h) on a pristine sample to quantify the effects of the XPS source on the crystals. We observed the appearance of a metallic lead (Pb^0) component in the spectrum as well as a decrease in in the Br/Pb ratio, in agreement with previous studies. [1,2] The N/Pb was unchanged during the experiment. These results fit well with the degradation mechanism proposed by Wang et al.[1] under X-rays and in UHV:

$$CH_3NH_3PbBr_3 \xrightarrow{X-ray} Pb^0 + CH_3NH_3Br + Br_2\uparrow \quad \text{in UHV}$$

After the first XPS scan the Pb0/Pb ratio is approximately 7%. Any metallic Pb^0 detected below this limit could be due to the XPS source itself rather than to other factors

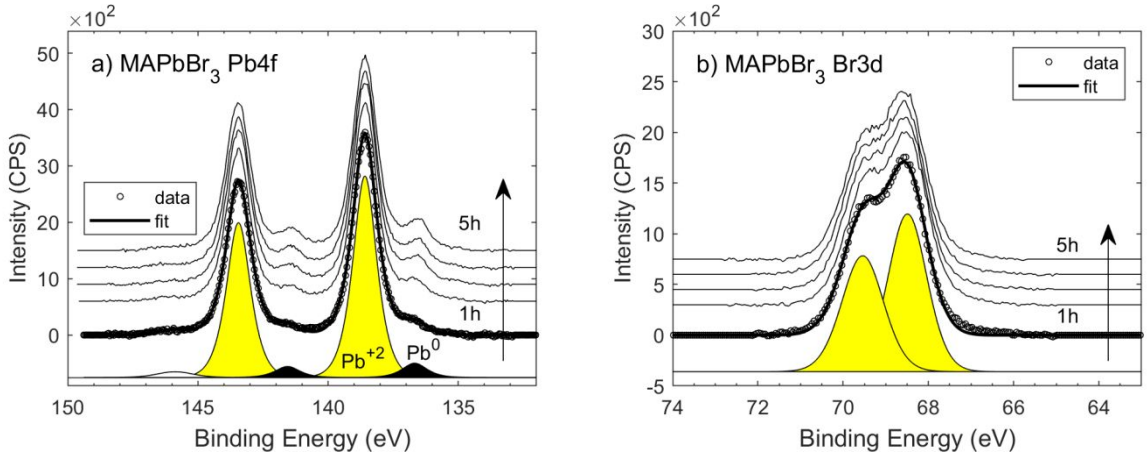

Figure S3. Time evolution during XPS calibration experiment to quantify the damage of the XPS beam on the crystals. Pb 4f and Pb^0 (a), and Br 3d doublet (b) are reported. The fitting curves are displayed in yellow for Pb^{+2} and Br 3d, and in black for Pb^0. An offset was added to the curves for clarity purpose.

Time	Pb^{2+} + Pb^0	Br	N	Pb^0/Pb	O/Pb
1h	1	2.8±0.1	1.2±0.1	0.067±0.009	0.04±0.02
2h	1	2.7±0.1	1.2±0.1	0.102±0.009	0.04±0.02
3h	1	2.6±0.1	1.1±0.1	0.127±0.009	0.035±0.02
4h	1	2.6±0.1	1.2±0.1	0.127±0.009	0.03±0.02
5h	1	2.6±0.1	1.2±0.1	0.140±0.009	0.05±0.02

Table S1. Elemental ratios in the $MAPbBr_3$ single crystal during XPS calibration experiment. All values are normalized to total Pb = Pb^0 + Pb^{+2} (column 2).

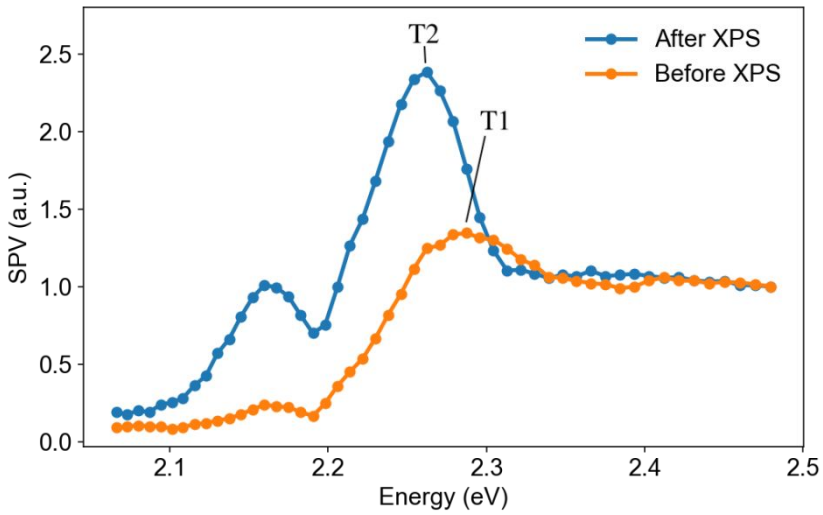

Figure S4. SPV spectra of the crystal used for the calibration experiment (orange line) and after (blue line) 4 repeated XPS scans of 1 hour. This shows that quenching of the T1 peak and the appearance of the T2 peak is observed also after irradiation in UHV conditions.

Elemental ratios as measured by XPS on samples irradiated with W target X-ray source in air

Dose (Gy)	Pb	Br	N	Pb^0/Pb (%)	O/Pb (%)
0	1.0	2.7 ±0.1	1.20 ±0.05	6.2	6.0
60	1.0	2.6 ±0.1	1.10 ±0.05	5.8	14.0
120	1.0	2.5 ±0.1	1.00 ±0.05	6.8	29.0
0 (7 days)	1.0	2.4 ±0.1	0.81 ±0.05	6.8	41.0
60 (7 days)	1.0	2.2 ±0.1	0.48 ±0.05	4.7	42.0
120 (7 days)	1.0	2.2 ±0.1	0.52 ±0.05	4.7	51.0

Table S2. Columns 2-4: relative concentration of Pb, Br and N for samples probed by XPS just after irradiation and after one week. The Pb signal includes both the Pb^0 and the Pb^{2+} contributions. Columns 5-6: percentual contribution of Pb^0 to the total Pb signal and percentual ratio of oxygen amount with respect to Pb, respectively.

References

(1) Wang, C.; Ecker, B. R.; Wei, H.; Huang, J.; Gao, Y. Environmental Surface Stability of the MAPbBr3 Single Crystal. *J. Phys. Chem. C* **2018**, *122* (6), 3513–3522. https://doi.org/10.1021/acs.jpcc.7b12740.

(2) Sadoughi, G.; Starr, D. E.; Handick, E.; Stranks, S. D.; Gorgoi, M.; Wilks, R. G.; Bär, M.; Snaith, H. J. Observation and Mediation of the Presence of Metallic Lead in Organic-Inorganic Perovskite Films. *ACS Appl. Mater. Interfaces* **2015**, *7* (24), 13440–13444. https://doi.org/10.1021/acsami.5b02237.