

# Dis-covering Self-Healing in Halide Perovskites

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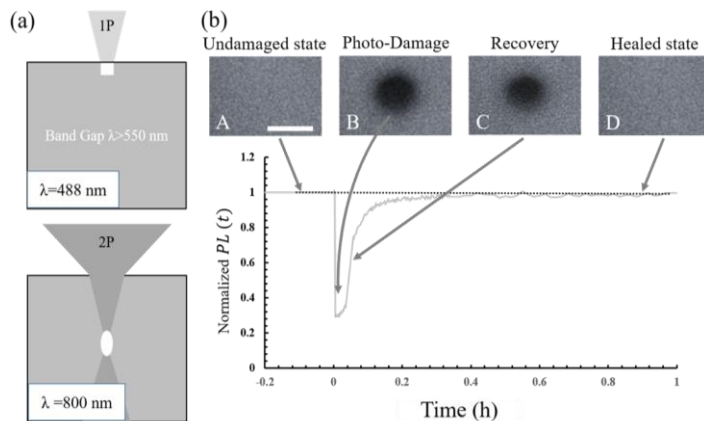
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There is considerable evidence that Halide Perovskites have, if prepared well, surprisingly low densities of optically and electronically active defects<sup>1-3</sup>.

One explanation that was proposed for this, is that these are self-healing materials, i.e., if some damage that degrades their optoelectronic properties is induced by light or particle beams, the materials can return to the *status quo ante*<sup>4</sup>, in a way that may be similar to what is known about another solar cell absorber, CuInSe<sub>2</sub> (and, by analogy, Cu(In,Ga)Se<sub>2</sub>, CIGS)<sup>4</sup>.

Here we report the results of our **experiments following the dynamics of defects and of degradation / curing processes *in situ***. We do so by studying the bromide perovskites APbBr<sub>3</sub>, where A = methylammonium (MA), formamidinium (FA) or cesium (Cs). We use single crystals, to study the pure materials without interference from interfaces, surfaces and subsequent effects, typical of many configurations, including solar cell ones. The time scales of the inspected phenomena vary over several orders of magnitude, are specific to each bromide perovskite and are affected by doping and composition, in addition to temperature and illumination.

To follow self-healing directly we use optical measurements that do not require interaction of the HaP with any other material except its ambient. We used furthermore two-photon (2P) absorption with 800 nm laser excitation, which is below the ( $\sim 2.2$ - $2.3$  eV, 530-570 nm) bandgap (to excite electrons inside the crystals. The 2-P technique allows excitation and probing the materials  $\sim 110$   $\mu\text{m}$  inside the crystal. This is impossible using supra-bandgap light, most of which is absorbed



**Figure 1:** From ref. 5: **(a)** Schematics of normal (one-photon, 1P-488 nm supra-bandgap) and two-photon, 2P (800 nm sub-bandgap) excitation. While the supra-bandgap light (1P) is absorbed by the halide perovskite within a few 100 nm (left), sub-bandgap light (2P) is absorbed only deep within the crystal around the focal point. **(b)** Damage and subsequent recovery dynamics of HaP sample in a FRAP experiment. Scale bar = 10  $\mu\text{m}$ . **A:** Image through 2P confocal microscope; average PL intensity is normalized to 1. **B:** photo-induced damage in defined area or volume of HaP single crystal in the bulk (2P). **C:** (PL signal) recovery, followed over min to hrs. **D:** if self-healing occurs, PL eventually recovers, partly or completely, depending on degree of self-healing.

100-200 nm from the surface (Figure 1a), which prevents probing the atmosphere-free light-matter interaction we want to study. We used the FRAP (Fluorescence Recovery After Photobleaching) protocol. Imaging was done with a scanning confocal microscope at low excitation intensity to detect the sample's photoluminescence, PL, without damaging it. In FRAP, damage is achieved by increasing the laser power during scanning to locally deposit a high amount of energy (i.e., photobleaching), which transforms the material. Consequently, when the sample is irradiated again at the imaging intensity, a change of PL is observed, which we associate with sample modification. A FRAP experiment is usually composed of 3 steps: 1-

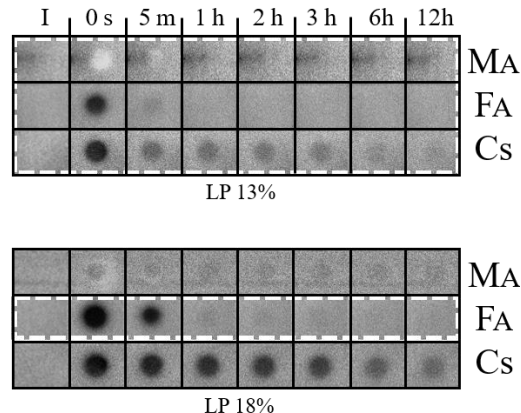
obtaining the PL image before damage (Figure 1b-A), which gives the reference PL signal. 2- cause damage (bleaching) with high laser power (Figure 1b-B); 3- monitor PL recovery over time (at imaging intensity) (Figure 1b-C-D).

In Figure 2 we show the 2P FRAP experiment on the three different materials. The initial pristine state is denoted by 'I'; the state immediately after photobleaching as '0 s' and the recovery states, according to the time after bleaching, '5 m', '1 h', '2 h', '3 h', '8 h', '12 h'. Each rectangular block corresponds to a different laser power in a single bleaching cycle, i.e., 13 and 18% of 120 mW (averaged power). The spots (~ 8  $\mu\text{m}$  diameter) result after a single bleaching cycle (1 iteration; 140 fs laser on, 12.5 ns laser off, pixel size 272 nm, pixel dwell 9.97  $\mu\text{s}$ ) of scanning with the 800 nm laser, focused at the diffraction limit.

At low power, all samples show striking healing after initial damage. MA reacts to bleaching with increasing intensity without PL peak shift, while FA and Cs show decreased intensity. The MA and FA samples return to their original state in minutes, but recovery of the Cs perovskite is slower. Increasing laser power, damage also increases and healing takes longer. Quantitative difference between lower laser power results is found for FAPbBr<sub>3</sub> and CsPbBr<sub>3</sub>, but overall the qualitative trend is similar – PL intensities decrease. In the case of MAPbBr<sub>3</sub>, however, at high intensity, the PL changes are opposite from those at lower intensities. Interestingly, in general, the most pronounced self-healing effect is obtained in FAPbBr<sub>3</sub> and NOT in CsPbBr<sub>3</sub>, which is normally considered the more stable HaP. These experiments prove directly the ability of the HaP to self-heal after photo-induced damage. Since in the past, only near-surface experiments were done, any self-healing was at least partially hidden by other phenomena resulting from contact with the ambient and, likely, also because of surface defects. Further studies of this kind are being performed while writing this long abstract, varying temperature and bleaching conditions<sup>5</sup>. Further work will include the iodide-based HaPs and if available, results will be included in the presentation, which will summarize the results, compare them to, and evaluate them against what is known (from the literature) to analyze the relations between the different timescales and the proposed damaging and restoration mechanisms<sup>6-8</sup>. I will emphasize light-induced damage as function of light intensity, time and temperature, and explore, analyze and conclude on the possible roles of ion migration.

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**Figure 2** : From ref. 5: 2P (800 nm) bleaching and recovery of APbBr<sub>3</sub> single crystals. Each horizontal set of squares of the rectangular blocks shows data for one of the three compounds, indicated (far left), as MA: MAPbBr<sub>3</sub>; FA: FAPbBr<sub>3</sub>; Cs: CsPbBr<sub>3</sub>. Each block corresponds to different laser power. Cases of (near) total recovery are indicated by dashed-lined white frames