**Interaction of oxygen with halide perovskites**

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**SUPPLEMENTARY INFORMATION**

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1) Methods

Synthesis

As a first step, MAI was obtained using the reported procedure by Im et al.\textsuperscript{[1]} MAPI thin films were synthesized in an Ar glove-box (P(O\textsubscript{2}) and P(H\textsubscript{2}O) < 0.1 ppm) by spin-coating sapphire substrates with an equimolar solution of MAI and PbI\textsubscript{2} (Alfa Aesar, 99.995\%) in DMSO (1.5 M). During the spin coating, a chlorobenzene drop was added to induce rapid crystallization and lead to compact films. Samples were annealed at 373 K for 5 min. For the electrical characterization, Au electrodes were previously deposited on Al\textsubscript{2}O\textsubscript{3} in an interdigitated fashion (Fig. S1) and subsequently covered with the MAPI film. Typical thickness of a film is around 300 nm.

![Fig. S1. Microscope image of interdigitated Au electrodes on an Al\textsubscript{2}O\textsubscript{3} substrate.](image)

For the pellets, MAPbI\textsubscript{3} single crystals were synthesized according to the procedure reported by Saidaminov et al.\textsuperscript{[2]} Synthesis was performed in laboratory air. Crystals were subsequently crushed under inert atmosphere (glove-box) and uniaxially pressed to achieve dense pellet. The pressing step yielded relative densities of around 95 \%. Typical thickness of a pellet is around 0.6 mm.

Tracer diffusion experiment:

The tracer diffusion experiment was performed as schematized in Fig. 1a. Samples (pellets or films) were loaded in a chamber, which was initially evacuated at room temperature to remove residual atmosphere. After this step, O\textsubscript{2} was introduced into the chamber (87\% \textsuperscript{18}O enrichment) and the samples were heated to the appropriate temperature. When necessary, light (Xe-arc lamp) was introduced onto the samples immediately after reaching the temperature. After the annealing step, the samples were quickly transfer to a ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectroscopy, model TOF.SIMS IV from IONTOF) instrument and a depth profile was
measured from the surface. During vacuum pumping, and whenever possible, the chamber was kept in the dark. For pellets, a 500x500 μm² area was probed, using a Ga primary gun (25 keV) and a Cs sputter gun (1 keV). For thin films, milder conditions were used, such as the Ga primary gun at 15 keV and the Cs sputter gun at 250 eV, probing a 70x70 μm² area.

The normalization of the oxygen content used in Fig. 1 is achieved with the following formula,\(^\text{[3]}\) which accounts for the natural abundance of the isotope and the enrichment used:

\[
c_{\text{norm}}(x,t) = \frac{c(x,t) - c_{\text{bg}}}{c_g - c_{\text{bg}}}
\]

Where the measured concentration \(c(x,t)\) is normalized by the natural abundance of the isotope used (\(c_{\text{bg}} = 0.2\%\) for \(^{18}\text{O}\)) and the isotope enrichment of the mixture used for the exposure (\(c_g = 85\%\) in our case). As measured concentration, we used the ratio between \(^{18}\text{O}\) and \(^{16}\text{O}\) SIMS signals. The samples for this experiment were prepared in the same batch and treated simultaneously under the same conditions, thus we expect to have a comparable starting concentration of oxygen. We note here once more that this experiment is more representative of a chemical diffusion than of a tracer diffusion process, due to the fact that oxygen is here an impurity and not a pristine lattice constituent. Finally, the analysis of the diffusion profile was performed using the following formula, and extracting the values for \(k^*\) and \(D^*\)\(^\text{[3]}\):

\[
\begin{align*}
    c_{\text{norm}}(x,t) &= \text{erfc}\left(\frac{x}{2\sqrt{D^* t}}\right) - \exp\left(\frac{k^* x}{D} + \frac{k^{*2} t}{D}\right) \cdot \text{erfc}\left(\frac{x}{2\sqrt{D t}} + k^* \sqrt{\frac{t}{D}}\right)
\end{align*}
\]

Several fit operations were tried for each plot, in order to confirm that indeed there are no significant variations of \(D^*\) with light intensity, but only of \(k^*\).

**Electrical measurements:**

Electrical characterizations were performed by means of DC-galvanostatic polarization. Experiments were conducted by using a current source (Keithley model 220) and by monitoring the voltage change with a high impedance electrometer (Keithley model 6514). Measurements were carried out by accurately controlling temperature and atmosphere over the sample (oxygen content and humidity were monitored using appropriate sensors). A Xe-arc lamp (Newport) was used for illumination; light was introduced through a quartz optical guide and the intensity calibrated with a power meter.
**UV-Vis measurements:**

Samples were measured using a Uvikon XL spectrometer. In order to measure films in transmission under controlled atmosphere, a normal quartz cuvette was adapted (Fig. S2). Temperature was controlled using heating pads perpendicular to the light transmission line. The samples were exposed to degradation conditions until full disappearance of the bandgap absorption signal. When no significant degradation was observed, the experiment was halted after 150 hours. The degradation progress was quantified from the absorption over the entire bandgap (fit as a sinusoidal curve), normalized to the initial value at t=0 (Fig. 3d). The illumination was normally provided by a QTH lamp (Thorlab SLS201L) or, for the wavelength dependence, by a red (660 nm, Thorlab M660F1) or violet (420 nm, Thorlab M420F2) LED.

**Iodine partial pressure control:**

To control P(I₂) over the samples, Argon was flown through a container with iodine chips, kept in a thermostat at fixed temperature (always below room temperature, typically between -50 °C and -10 °C). Iodine partial pressure was assumed to correspond to the equilibrium pressure of iodine at the thermostat temperature, which was calculated based on the equation from Ref.[4]. Note that similar values are obtained by estimating P(I₂) purely from thermodynamic considerations, starting from the Gibbs free energy of sublimation of solid iodine (and values calculated from data taken from Ref.[5]).

**X-Ray Diffraction:**

XRD patterns were obtained by using a PANalytical Empyrean Series 2 (Cu Kα radiation, 40 kV, 40 mA) in grazing incidence (ω=2°) equipped with a PIXcel3d detector and focusing mirror. To avoid degradation during measurements, samples were analyzed in a sample holder equipped with a gas-tight polycarbonate dome (Anton Paar), sealed under Ar in a glove box. For the in-situ degradation monitoring, the sealed dome was equipped with gas tubes and an optical fiber connector. Grazing-incidence XRD were recorded every 2 hours, under constant gas flow, at room temperature and with illumination provided by a LED light (6200 K, Thorlab MCWHF2).

**Light Intensity:**

For all the previous measurements, light intensity was directly measured with a thermal power meter (ORIEL 70260, with probe 70261).
2) Thermodynamic considerations

Table 1. Standard formation enthalpy, entropy and Gibbs energy of halide perovskites from various references. All standard entropies of formation were calculated using \( S^0 \) values extracted from Ref. [6].

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta_f H^{0}_{298K} ) (kJ mol(^{-1}))</th>
<th>( \Delta_f S^0 ) (J mol(^{-1}) K(^{-1}))</th>
<th>( \Delta_f G^{0}_{298K} ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{NH}_3\text{PbI}_3 )</td>
<td>-375.7(^{[7]})</td>
<td>-358.6(^{[6]})</td>
<td>-268.8</td>
</tr>
<tr>
<td></td>
<td>-341.6(^{[6]})</td>
<td></td>
<td>-234.7</td>
</tr>
<tr>
<td></td>
<td>-371.6(^{[6]})</td>
<td></td>
<td>-264.7</td>
</tr>
<tr>
<td>( \text{CH}_3\text{NH}_3\text{PbBr}_3 )</td>
<td>-539.6(^{[7]})</td>
<td>-437.6(^{[6]})</td>
<td>-409.1</td>
</tr>
<tr>
<td></td>
<td>-529.6(^{[6]})</td>
<td></td>
<td>-399.1</td>
</tr>
<tr>
<td></td>
<td>-543.1(^{[6]})</td>
<td></td>
<td>-412.6</td>
</tr>
<tr>
<td>( \text{CH}_3\text{NH}_3\text{PbCl}_3 )</td>
<td>-660.5(^{[7]})</td>
<td>-579.9(^{[6]})</td>
<td>-487.6</td>
</tr>
<tr>
<td></td>
<td>-666.7(^{[6]})</td>
<td></td>
<td>-493.8</td>
</tr>
<tr>
<td></td>
<td>-662.2(^{[6]})</td>
<td></td>
<td>-489.3</td>
</tr>
</tbody>
</table>

Table 2. Standard formation enthalpy, entropy and Gibbs energy of various compounds, taken from Ref. \(^{[10]}\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta_f H^{298K} ) (kJ/mol)</th>
<th>( \Delta_f G^{298K} ) (kJ/mol)</th>
<th>Compound</th>
<th>( \Delta_f H^{298K} ) (kJ/mol)</th>
<th>( \Delta_f G^{298K} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3\text{NH}_2 ) (^{(g)})</td>
<td>-22.5</td>
<td>32.8</td>
<td>( \text{PbI}_2 ) (^{(s)})</td>
<td>-175.5</td>
<td>-173.6</td>
</tr>
<tr>
<td>( \text{CH}_3\text{NH}_3 ) (^{(g)})</td>
<td>-200.7</td>
<td>-83.9</td>
<td>( \text{PbBr}_2 ) (^{(s)})</td>
<td>-278.7</td>
<td>-261.9</td>
</tr>
<tr>
<td>( \text{HI} ) (^{(g)})</td>
<td>0.0</td>
<td>0.0</td>
<td>( \text{H}_2\text{O} ) (^{(g)})</td>
<td>-241.8</td>
<td>-228.6</td>
</tr>
<tr>
<td>( \text{HBr} ) (^{(g)})</td>
<td>-36.3</td>
<td>-53.4</td>
<td>( \text{H}_2\text{O} ) (^{(l)})</td>
<td>-285.8</td>
<td>-237.1</td>
</tr>
<tr>
<td>( \text{HCl} ) (^{(g)})</td>
<td>-92.3</td>
<td>-95.3</td>
<td>( \text{O}_2 ) (^{(g)})</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>( \text{I}_2 ) (^{(g)})</td>
<td>62.4</td>
<td>-15.3</td>
<td>( \text{PbO} ) (^{(s)})</td>
<td>-217.30</td>
<td>-187.90</td>
</tr>
<tr>
<td>( \text{I}_2 ) (^{(s)})</td>
<td>0.0</td>
<td>0.0</td>
<td>( \text{CH}_3\text{NH}_3\text{Br} ) (^{(s)})</td>
<td>-258.90</td>
<td></td>
</tr>
<tr>
<td>( \text{Br}_2 ) (^{(g)})</td>
<td>0.0</td>
<td>0.0</td>
<td>( \text{CH}_3\text{NH}_3\text{Cl} ) (^{(s)})</td>
<td>-298.30</td>
<td>-159.20</td>
</tr>
</tbody>
</table>

Table 3. Degradation reactions for MAPbI\(_3\). MAPbI\(_3\) thermodynamic data taken from Ref. \(^{[9]}\).

<table>
<thead>
<tr>
<th>Degradation reaction for MAPbI(_3)</th>
<th>( \Delta_f G^{298K} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Eq. S1) ( \text{CH}_3\text{NH}_3\text{PbI}_3 \rightarrow \text{CH}_3\text{NH}_3\text{I} + \text{PbI}_2 )</td>
<td>7.2</td>
</tr>
<tr>
<td>(Eq. S2) ( \text{CH}_3\text{NH}_3\text{PbI}_3 \rightarrow \text{CH}_3\text{NH}_2 + \text{HI} + \text{PbI}_2 )</td>
<td>129.7</td>
</tr>
<tr>
<td>(Eq. S3) ( \text{CH}_3\text{NH}_3\text{PbI}_3 \rightarrow \text{CH}_3\text{NH}_2 + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{I}_2 + \text{PbI}_2 )</td>
<td>128.0</td>
</tr>
</tbody>
</table>
\[
\text{(Eq. S4)} \quad \text{CH}_3\text{NH}_3\text{PbI}_3 + \frac{1}{4} \text{O}_2 \rightarrow \frac{1}{2} \text{H}_2\text{O} + \text{CH}_3\text{NH}_2 + \text{PbI}_2 + \frac{1}{2} \text{I}_2 \quad \Delta_r G^{0}_{298K} = 5.3 \text{ kJ/mol}
\]

\[
\text{(Eq. S5)} \quad \text{CH}_3\text{NH}_3\text{PbI}_3 + \frac{3}{4} \text{O}_2 \rightarrow \frac{1}{2} \text{H}_2\text{O} + \text{CH}_3\text{NH}_2 + \text{PbO} + \frac{3}{2} \text{I}_2 \quad \Delta_r G^{0}_{298K} = -9.0 \text{ kJ/mol}
\]

Table 4. Degradation reactions for MAPbBr\textsubscript{3} and MAPbCl\textsubscript{3} involving O\textsubscript{2}. Thermodynamic data for halide perovskites taken from Ref. [9].

<table>
<thead>
<tr>
<th>\text{O}_2 \text{ degradation for different halide perovskites}</th>
<th>\Delta_r G^{0}_{298K} / (\text{kJ/mol})</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{(Eq. S6)} \text{CH}_3\text{NH}_3\text{PbBr}_3 + \frac{1}{4} \text{O}_2 \rightarrow \frac{1}{2} \text{H}_2\text{O} + \text{CH}_3\text{NH}_2 + \text{PbBr}_2 + \frac{1}{2} \text{Br}_2</td>
<td>64.9</td>
</tr>
<tr>
<td>\text{(Eq. S7)} \text{CH}_3\text{NH}_3\text{PbCl}_3 + \frac{1}{4} \text{O}_2 \rightarrow \frac{1}{2} \text{H}_2\text{O} + \text{CH}_3\text{NH}_2 + \text{PbCl}_2 + \frac{1}{2} \text{Cl}_2</td>
<td>89.4</td>
</tr>
</tbody>
</table>

The degradation reaction of MAPbI\textsubscript{3} with O\textsubscript{2} shows that H\textsubscript{2}O, CH\textsubscript{3}NH\textsubscript{2} and I\textsubscript{2} are formed (Eq. S4). A Gibbs energy of reaction of +5.3 kJ/mol is obtained considering the components in their standard state. However, in a dynamic environment (i.e., under gas flow), water and iodine are likely to be present in gas form, due to the fact that they can be readily removed and their partial pressure can be rather small. For this reason, the decomposition reaction can be easily realized. Indeed, assuming a reasonable partial pressure of water of 10\textsuperscript{−3} bar (3% RH at room temperature), and of iodine and methylamine of 10\textsuperscript{−7} bar we obtain an overall $\Delta_r G$ of -66.7 kJ/mol under 1 bar of oxygen, i.e. a significantly favorable energy gain for decomposition. Under such products partial pressures, that are in a practical range of feasibility, thermodynamic stability can be barely reached only with an oxygen partial pressure of 10\textsuperscript{−47} bar ($\Delta_r G$= +0.46 kJ/mol), that is obviously practically impossible to achieve. The situation, however, is different considering for example MAPbBr\textsubscript{3}. Under an analogous assumption (P(H\textsubscript{2}O)=10\textsuperscript{−3} bar, P(Br\textsubscript{2}) = P(CH\textsubscript{3}NH\textsubscript{2}) = 10\textsuperscript{−7} bar) samples should be slightly stable even at 1 bar of oxygen ($\Delta_r G$= +0.7 kJ/mol). MAPbCl\textsubscript{3} is also stable under such conditions (P(H\textsubscript{2}O)=10\textsuperscript{−3} bar, P(Cl\textsubscript{2}) = P(CH\textsubscript{3}NH\textsubscript{2}) = 10\textsuperscript{−7} bar), with a $\Delta_r G$= 25.1 kJ/mol.
3) Defect model of oxygen incorporation

We develop here a simple defect-chemical model for oxygen incorporation in MAPI. For the following derivation, we assume incorporation of atomic oxygen species on an iodine site, forming a substitutional defect $O_I^-$: The same derivation can be carried out for interstitial incorporation of oxygen ($O''_I$), and the results are qualitatively identical (but diverge quantitatively due to the difference in charge between the two defects, see Fig. S2). As stated in the main text, the large size of I$^-$ ions results in a spacious lattice that could accommodate the relatively small oxygen impurities interstitially. The situation is naturally different when considering the intrinsic defects, since perovskite materials, due to the dense structure, prefer the formation of intrinsic anion/cation vacancies rather than interstitials. We expect this to be the case also for MAPI. The intrinsic defect situation can thus be described by the Schottky equilibrium (here ignoring Pb defects, which are expected to have comparatively high formation energies):

$$\text{MA}_3^+\text{I}_2^- + I^- \rightleftharpoons V_I^+ + V_{\text{MA}}^- + \text{MAI}$$  \hspace{1cm} (Eq. S8)

Nonetheless, should other ionic disorder reactions with iodine vacancies be in majority, this would not change the picture significantly. The intrinsic material, even in the absence of $O_2$, must be in equilibrium with the external atmosphere, thus its vacancy concentration will depend on the partial pressure of the relevant exchangeable component ($I_2$ in this case):

$$\frac{1}{2} I_2 + V_I^- \rightleftharpoons I_I^- + h^+ \hspace{1cm} K_i = \frac{[h^+]}{[V_I^-]P_{I_2}}$$  \hspace{1cm} (Eq. S9)

Furthermore the $O_2^–$-incorporation on the anion vacancy, which is coupled with the formation of electron holes, can be written as:

$$\frac{1}{2} O_2 + I_I^- \rightleftharpoons O_I^+ + h^+ + \frac{1}{2} I_2 \hspace{1cm} K_o = \frac{[h^+][O_I^+]P_{I_2}^{1/2}}{P_{O_2}^{1/2}}$$  \hspace{1cm} (Eq. S10)

We expect Eq. S8 to dominate for low $O_2$ partial pressure, leading to an intrinsic defect situation where $[V_I^-]=[V_{\text{MA}}^-]$. Note that in this situation oxygen is still incorporated, but does not perceptibly affect the intrinsic concentrations (left region of diagram, Fig. S2a). Upon increasing $P(O_2)$, the concentration of $O_I^-$ in the bulk might increase to the point that it overcomes the intrinsic
situation (left region of diagram, Fig. S2a). Then, $O_1$ is dominant and we expect that $[V_{i}^*]=\left[O_{1}\right]$. This is analogous to acceptor doping, where increasing the concentration of $O_1$ results in an increase of $\left[V_{i}^*\right]$ and $[h^+]$. One important note is that this model is calculated for constant $P(I_2)$ in Eq. 9. When iodine partial pressure is not fixed by external means (e.g. under Ar), exposing MAPI to $O_2$ results in directly influencing $P(I_2)$, since incorporation of $O_2$ must be accompanied by $I_2$ loss from the sample, as dictated by Eq. S10. This is relevant for the observed $O_2$ influence on the electrical properties under dark, namely under conditions in which we would not expect the concentration of $O_1$ to overcome the intrinsic situation. Indeed, as shown in the main text, fixing iodine partial pressure eliminates this effect. On the other hand, when the concentration of $O_1$ is high enough to achieve perceptible doping, we expect the electrical properties to heavily change with $P(O_2)$, which was directly observed under illumination (Fig. 2b, Fig.S5). Based on Eq. S10, we also expect that a significant $P(I_2)$ will hinder oxygen incorporation, thus decreasing the concentration of $O_1$ and increasing the $P(O_2)$ necessary to achieve doping. This was also observed experimentally (Fig. 2e). We also note in this respect that, if the newly formed oxygen defect is strongly associated with the iodine vacancy (see Supplementary Section 5), a higher O-content is necessary also in this case to achieve doping. As a last comment, we recognize that this defect model relies on the formation of an equilibrium between the various components of the aforementioned equations. While this can be safely assumed in the dark, the steady-state situation under illumination does not allow for such a strict assumption, therefore in this respect we limited ourselves to qualitative considerations.

Fig. S2. Kröger-Vink diagram of defect concentrations as a function of $P(O_2)$ for MAPI. The diagrams are obtained under the assumption that atomic oxygen is incorporated (a) substitutionally on iodine site or (b) interstitially.
4) XRD of films after tracer experiment

We have performed XRD on the films treated in $^{18}$O$_2$ after the tracer experiment. The treatment was mild enough that almost no degradation was observed for any of the films. As a reference, Fig. S3 shows the diffractogram of the film treated under the strongest light intensity (1 mW/cm$^2$) and that showed the highest O$_2$ uptake. As visible, a very weak presence of PbI$_2$ is detectable, only in certain orientations. The vast majority of the sample has not degraded during the treatment.

![XRD of a MAPI film after tracer experiment. The one exposed to the strongest light intensity, giving the highest oxygen uptake, was taken as representative. Almost no degradation is visible.](image)

**Figure S3.** XRD of a MAPI film after tracer experiment. The one exposed to the strongest light intensity, giving the highest oxygen uptake, was taken as representative. Almost no degradation is visible.
5) Tracer impurity motion of oxygen in MAPbI$_3$

A formal detailed treatment of surface rate constants and diffusion coefficients based on detailed kinetics is given in Ref. [11]. Even though we use an isotope for better detection, the measured diffusion coefficients is a chemical diffusion coefficient ($D^\delta$). Here we will show that such impurity diffusion coefficient, which is characterized by the counter diffusion of oxygen and iodine, is sensitive to the bulk defect concentration if the impurity ($O_1^-$) migrates rather independently from the counter defect ($V_1^*$), but that $D^\delta$ is insensitive if there is strong association between them.

The motion of $O_1^-$ from $x$ to $x'$ can be written as a bimolecular reaction as:

\[
O_1^-(x) + V_1^+(x') \rightleftharpoons O_1^-(x') + V_1^+(x) \quad \text{(S11)}
\]

with the flux:

\[
\dot{j}_\delta = j^+ \propto \tilde{k}[O_1][V_1^+] - \tilde{k}[O_1^+][V_1^-] \quad \text{(S12)}
\]

where $\tilde{k} = \tilde{k}$.

If the background vacancy concentration is comparatively large, then $[V_1^+] = [V'_1^+]$ and $\dot{j}_\delta = [V'_1^+]V_c^*$, with $D^\sigma \propto [V'_1^+]$. The picture is complicated by the fact that the bulk incorporation of oxygen also produces iodine vacancies that are to be transported. Nonetheless in the above limit, the result is the same. (Note that an ambipolar motion of $O_1^-$ and $V_1^*$ yields $D^\delta \propto u_{O_1}^*$ if $\sigma_{V_1^*}$ and $c_{V_1^*}$ are large, with $u_{O_1}^* \propto c_{V_1^*}$ as the vacancy is the jump partner for the oxygen defect).

The situation is obviously very different if the $O_1^-\cdot V_1^*$ couple forms a highly bound pair, as expected for room temperature (and also experienced with oxide perovskites). In such a case the diffusion is determined by the pair itself:

\[
(O_1^-\cdot V_1^*) (x) \rightleftharpoons (O_1^-\cdot V_1^*) (x') \quad \text{(S13)}
\]

and

\[
\dot{j}^* \propto \dot{j}_{(O_1^-\cdot V_1^*)} = \text{const.} V_c^* \quad \text{(S14)}
\]
where \( \text{const.} \) means constant with respect to bulk concentration.

This explains the insensitivity of \( D^i \) with respect to \( [V_i^*] \) as referred to in the main text. Note that the jump rate constant (mobility) of the pair motion is in itself not simple, as pointed out in Fig. S4, but that this conclusion applies as long as \( [V_i^*] \) is not too large.

A detailed mechanistic treatment of impurity diffusion was given by Lidiard.\(^{[12]}\) The fact that the process formulated above is not an elementary reaction (Eq. S13) (for which a simple rate expression cannot be expressed), means that the conclusion given in Eq. S14 will apply as long as no additional vacancy is involved.

![Fig. S4. Schematic of correlated pair motion. The vacancy is generated by the incorporation of the O-defect. No extra bulk vacancy is needed for the motion to take place.](image-url)
6) Conductivity of MAPI films as a function of $P(O_2)$ under higher light intensity

As a further verification of the results obtained from the electrical measurements shown in Fig. 2b, DC-galvanostatic polarization as a function of $P(O_2)$ was measured at a higher light intensity (Fig. S5). The behavior is in full agreement with the experiment performed at lower light intensity and presented in the main text.

**Figure S5.** Conductivity measurements as a function of oxygen pressure (Ar as carrier gas) for MAPI thin films at 333 K. Ionic and electronic contribution to the conductivity extracted from d.c. galvanostatic polarization under 1.75 mW/cm$^2$ illumination. Electronic conduction is severely affected by $O_2$ exposure under illumination. Ionic conduction is initially unaffected but at higher $P(O_2)$ values also increases under illumination. Interestingly, this process is reversible upon removal of light.
7) Reversibility of electrical measurements

The changes generated by oxygen exposure under the mild conditions of the electrical characterization were fully reversible. To confirm this, we recorded the transport properties before and after O\textsubscript{2} treatment. As shown in Fig. S6, no significant variation is present, nor in dark nor under illumination, after the entire O\textsubscript{2} partial pressure curve was recorded. Also, no color changes or microstructural modifications were present after the treatment.

![Figure S6. Electrical transport properties of a MAPI film before and after being exposed to several O\textsubscript{2} partial pressures in order to record the curves of Fig. 2 (main text). The full measurement took more than 3 weeks (> 500 hours) to be completed. Still, no significant changes are visible, both in dark and under the two light intensity used, indicating that the sample was stable under the treatment conditions.](image-url)
8) Conductivity equilibration upon changing P(O₂) in MAPI films

The analysis of the equilibration processes caused by changing the oxygen partial pressure over a sample gives information on the underlying interaction/incorporation process. As a first observation, the equilibration times are much slower in the dark, and appear to scale with light intensity (Fig S7), in agreement with the tracer diffusion results reported in the main text. Interestingly, even though the samples are already equilibrated at a certain P(O₂) in the dark, upon illumination an additional equilibration process is observed (Fig. S7). The time scales of this process under illumination are significantly faster than in the dark (5x and 10x when using 0.5 and 1.75 mW/cm² light intensity, respectively). Upon switching off the light, the sample re-equilibrates to its initial value of conductivity in dark, with a slow time scale. These results indicate that the stoichiometry of MAPI is indeed affected by oxygen exposure, particularly under light. In addition, the changes obtained by simultaneously exposing the samples to light and O₂ persist for long time after removing the illumination, in agreement with a “quenching” of a high O₂ content in MAPI previously quickly incorporated under light (see tracer experiments).

We note that curiously the equilibration under dark upon increasing P(O₂) shows a decrease for the electronic conductivity (increase for the ionic) while we would expect an opposite behavior (and no change for ionic), as shown in Fig. 2a. However, when comparing this trend to the initial value before increasing P(O₂) (given in Fig. S7, Dark) one recognizes that the absolute value of the electronic conductivity is increasing after equilibration, and the one of the ionic remaining constant, as expected. However, there is an initial process upon changing P(O₂) that gives a quick increase of the electronic value, while simultaneously suppressing the ionic value. The nature of this process is presently unknown, but might be due to several (possibly simultaneous) reasons, such as temporary local variations of partial pressures and temperature caused by switching gases. Under light, a similar behavior is also observed, albeit here only the electronic conductivity behaves unexpectedly.
Figure S7. Equilibration of the ionic and electronic contribution to the conductivity of MAPbI₃ film exposed to the abovementioned conditions. The treatments were performed in sequence. First, a sample kept at 10 mbar P(O₂) in the dark was exposed to 100 mbar, maintaining dark conditions (conductivity values at 10 mbar given). Then, after equilibration, we turned on the light, initially with lower intensity and then with higher. Finally, we removed the illumination, still keeping the same P(O₂). The same behavior was observed upon any change of oxygen partial pressure. Conductivity data are obtained by DC-galvanostatic polarization measurements with ion-blocking Au electrodes. Time scales ($t^δ$) extracted from the logarithmic equilibration process are given in the graph.
9) In-situ UV-Vis under pure Ar and Ar + P(I₂)

As a reference measurement, we performed UV-Vis spectroscopy on a MAPI film exposed to Ar under illumination at 333K, i.e. the same conditions used for O₂-degradation. As shown in Fig. S8a, after 1 week no degradation can be observed.

Moreover, in the interest of checking whether iodine partial pressure alone is harmful for the sample, we exposed a film to iodine partial pressure, temperature and light simultaneously. As seen in Fig. S8b, almost no degradation was visible in these conditions after more than 100 hours. Interestingly, a small tail at high wavelengths is visible, indicating amorphization of the sample. Further studies are needed to confirm and better investigate this behavior.

**Figure S8.** In-situ UV-Vis absorption of a MAPI film under (a) pure Ar and (b) Ar and iodine partial pressure (P(I₂) = 1.4·10⁻⁵ bar). Both samples were kept under 4.6 mW/cm² light and at 333 K.
Degradation study with XRD

As complement to the data presented in Fig. 4, here we give the full XRD pattern of MAPI samples before and after exposure to different conditions. As shown in Fig. S9, in the dark almost no degradation is detected after 70 hours, as clear from the very intense (and practically unvaried) MAPI peaks. Nonetheless, a small formation of PbI$_2$ is still present, particularly in certain crystal orientations. Under illumination, full phase conversion to PbI$_2$ is observed, and no MAPI peaks are visible after degradation. Interestingly, one recognizes that under simultaneous oxygen and iodine exposure, degradation is not only slowed down, but also almost no PbI$_2$ reflections are generated afterwards. Since we observe a color change from dark to yellow, as expected, and since almost no MAPI peaks are left, we attribute this observation to a complete degradation of MAPI to an amorphous PbI$_2$ phase.

**Figure S9.** XRD of MAPI films before and after 70 hours exposure to (a) O$_2$ under dark (b) O$_2$ under illumination (43 mW/cm$^2$) and (c) O$_2$ and I$_2$ ($P$(I$_2$) = 4.5·10$^{-6}$ bar) under illumination (43 mW/cm$^2$). All characterizations were performed in-situ at room temperature.
Degradation of mixed (MA,FA) cation perovskites

As a final step, the degradation of a mixed cation formulation \(((\text{MA}_{0.8}\text{FA}_{0.2})\text{PbI}_3)\) was analyzed. As shown in Fig. S10, here a degradation process is also observed, but less rapid than for pure MAPI. Even though a significant part of the sample is degraded, no PbI$_2$ peaks are present. The reason that we do not observe reflections of reaction products we attribute to the following points: formation of amorphous PbI$_2$ and formation of pure FAPbI$_3$, that at room temperature is stable in a $\delta$-phase with very weak XRD.$^{[13]}$ The analysis of the UV-Vis absorption in the main text is quantitatively in agreement with the observed decrease in intensity of the XRD reflections. Moreover, in this analysis we observe the formation of a tail in the absorption, which can be attributed to a loss of crystallinity of the perovskite phase.

![Figure S10. XRD analysis of \((\text{MA}_{0.8}\text{FA}_{0.2})\text{PbI}_3\) under O$_2$ exposure and 43 mw/cm$^2$ illumination, measured at room temperature. (a) Full diffraction pattern before and after treatment. (b) Comparison between the degradation of pure MAPbI$_3$ and of \((\text{MA}_{0.8}\text{FA}_{0.2})\text{PbI}_3\) under O$_2$ exposure, monitored with XRD under illumination (43 mW/cm$^2$) at room temperature. The points are obtained from the normalized intensity of the strongest reflection, which is found at 14.1° 2θ for both compositions.](image-url)
12) Ionic conductivity of $\text{MA}_{0.8}\text{FA}_{0.2}\text{PbI}_3$

To explain the enhanced stability of mixed cation MOIHPs, we studied the ionic conductivity by means of DC-galvanostatic polarization. As reported in Fig. S11, mixing FA with MA reduces the ionic conductivity by half an order of magnitude with respect to the pure MAPbI$_3$, and this is in agreement with the observed slower degradation process.

![Ionic conductivity graph](image)

**Figure S11.** Ionic and electronic conductivity of MAPbI$_3$ and $\text{MA}_{0.8}\text{FA}_{0.2}\text{PbI}_3$, measured by DC-polarisation at 333 K under Ar atmosphere. Ionic conductivity is hindered in the cation mixture.
13) Analysis of possible fast grain boundary diffusion

We analyze here the possibility of having a fast grain boundary diffusion of oxygen in MOIHPs, and the resulting signature in the tracer diffusion profiles (Fig. 1). For this analysis, it is necessary to plot the logarithm of the normalized tracer concentration (c'). A bulk diffusion profile is expected to have a convex shape with depth, and we observe indication of such behavior in Fig. S12a, albeit slightly. Moreover, we can analyze our tracer diffusion profile under the assumption of fast grain boundary diffusion.\[^{14-17}\] For comparatively fast grain boundary diffusion one would expect to observe two linear regions in the ln(c') vs depth\(^{6/5}\) plot. However, as shown in Fig. S12b, we clearly only observe one region. This either means that the entire process is dominated by bulk diffusion, or that it is fully dominated by fast grain boundary diffusion. As stated in the main text, the observation of a doping process clearly indicates we are dealing with a bulk diffusion process. We note that, even in the event of fast grain boundary diffusion, our main conclusions would not be affected.

![Figure S12](image)

**Figure S12.** Plot of the natural logarithm of the normalized tracer concentration (c') obtained from a MAPbI\(_3\) film annealed in \(^{18}\)O under 1 mW/cm\(^2\) illumination. (a) Plot versus depth, to verify the expected decrease (indicated by the fit in the red line). (b) Plot versus depth\(^{6/5}\), where competitively fast grain boundary diffusion would result in two linear regions.
Photoluminescence study

Photoluminescence (PL) studies under pure oxygen have already been reported in the literature\textsuperscript{[18–21]} and discussed in the main text. Yet, the effect of simultaneous iodine exposure on the photoluminescence response under oxygen was never investigated. As shown in Fig. S13, pure oxygen exposure induces a reversible increase in the PL response, in agreement with literature\textsuperscript{[18–21]}. Interestingly, as reported in Fig. S14, simultaneous iodine exposure instead induces a significant (and still reversible) PL decrease with respect to pure oxygen. These results are consistent with our conclusion, in that iodine can prevent oxygen interaction, and thus also impede the photoluminescence enhancement induced by oxygen.

Figure S13. Photoluminescence response of a MAPbI\textsubscript{3} film under the indicated atmosphere.

Figure S14. Photoluminescence response of a MAPbI\textsubscript{3} film under the indicated atmosphere. With respect to the previous figure, a lower gas flow rate and light intensity were used in order to ensure stability, thus the PL enhancement results weaker.

We note that this experiment is not expected to give us any mechanistic insight on the oxygen interaction, as the PL response in halide perovskites is heavily affected by processes taking
place in the surface layer, due to the extremely high absorption coefficient of these compounds, making any conclusion on bulk processes challenging. Also, the high instability of these compounds to oxygen exposure makes it difficult to measure photoluminescence and simultaneously guarantee no degradation of the material, and this is an extremely relevant issue due to the known influence of the degradation product PbI$_2$ on the PL response.[22–25]

15) **Mixed cation perovskites with high FA content**

We performed degradation studies on a MA$_{0.2}$FA$_{0.8}$PbI$_3$ perovskite, with the intent of investigating a formulation that is closer to the ones used in state of the art devices. Due to a different viscosity of the precursor solution, the films made with this formulation were significantly thinner than the one reported in the main text (150 vs 300 nm). For a fair comparison, we synthetized equally thin MA$_{0.8}$FA$_{0.2}$PbI$_3$ films. As shown in Fig. S15a, as expected, the 80 % FA mixture appear more stable than the 20 % FA formulation. We note once again that in this case, the sample may not be phase pure, as known for high FA content mixtures.[26] Note also that the formation of pure, yellow-phase FAPbI$_3$ (either due to de-mixing or to partial degradation) would cause an initial degradation of the absorption followed by a hindered degradation rate due to passivation of the mixture by the more stable FAPbI$_3$ phase, in agreement with what is observed here. This is likely to be more relevant for high FA contents. Based on this, whether the observed enhanced stability with FA content is due to the chemistry or to parallel passivation processes is something that will have to be investigated elsewhere.

![In-situ UV-Vis absorption of different halide perovskite films under oxygen. All samples were kept under 4.6 mW/cm$^2$ light and at 333 K. (a) Different FA contents (thickness = 150 nm). (b) 20 % FA mixtures with different thicknesses.](image)

Figure S15. In-situ UV-Vis absorption of different halide perovskite films under oxygen. All samples were kept under 4.6 mW/cm$^2$ light and at 333 K. (a) Different FA contents (thickness = 150 nm). (b) 20 % FA mixtures with different thicknesses.
As an additional comment, we now can compare the same formulation (MA<sub>0.8</sub>FA<sub>0.2</sub>PbI<sub>3</sub>) with 2 different thicknesses. As shown in Fig. S15b, thicker films show a rather enhanced stability. While this observation is entirely expected, it confirms once again the bulk nature of the oxygen interaction.

16) Incorporation of O<sub>2</sub>: superoxide or oxide ions

We note that our experiments indicate that oxygen incorporation and dissolution in MAPbI<sub>3</sub> happens in the form of oxide ions rather than superoxide species.<sup>[27,28]</sup> Our reasoning is the following: (i) Molecular oxygen species normally have much lower solid-state diffusivity with respect to atomic species, simply due to size and shape considerations. (ii) If superoxide species would, as proposed, occupy iodine vacancies,<sup>[28]</sup> no heterovalent doping effect would be achieved, in clear contrast with our experimental observations (Fig. 2). (iii) The degradation path implies deprotonation of MA cations, forming volatile methylamine.<sup>[27]</sup> Based on simple considerations on the basicity, oxide ions are expected to be much more efficient in such endeavor. (iv) As we previously discussed (Fig. 1), tracer diffusion results show that oxygen is present in the bulk of a film after turning off the light (or even in a pellet kept under dark) and after exposing the samples to high vacuum for several hours (as necessary before measuring ToF-SIMS); this indicates that oxygen is incorporated in a stable form that does not require illumination to be maintained. Therefore, we suggest that formation of superoxide ions is likely an intermediate preceding step towards a full reduction to O<sup>2-</sup>, rather than present in perceptible concentration in MOIHPs. This intermediate formation also refer to degradation conditions, since the kinetic mechanism behind phase decomposition is expected to involve reactive intermediates such as superoxide species (as it is the case for perovskites at high temperatures),<sup>[29]</sup> while leaving the thermodynamic picture unchanged. Study of the kinetics of all the intermediate degradations steps is, however, beyond the scope of this work.
References:


