X-ray dose effects and strategies to mitigate beam damage in metal halide perovskites under high brilliance X-ray photon source

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Abstract

Metal halide perovskites are versatile photovoltaic and optoelectronic materials. However, they suffer from photo-structural-chemical instabilities whose intricacy requires state-of-the-art tools to investigate their properties and behavior under various conditions. In most cases, those tools strongly interact with the materials leading to undesirable transformations. This study addresses the damage caused by highly intense focused X-ray beams on hybrid organic-inorganic metal halide perovskites through a correlative multi-technique approach. Our results reveal that the damage after irradiation in the ((Cs, FAMA)Pb(Br, I)3) compound is prominent on iodine and organic components at the film surface, reducing their relative quantity. The sample morphology modifies with the formation of an excavated area, whose altered local optical properties indicate the formation of an optically inactive metal layer covering the surface. Interestingly, the bulk remains unaltered with the initial ion proportion demonstrated by the stable photoluminescence emission energy. Controlling the X-ray beam dose and environment - air, nitrogen, and cryogenic conditions - serves as a strategy to mitigate the dose harm. Hence, we combined a controlled X-ray dose with an inert N2 atmosphere to certify the conditions to probe metal halide perovskite properties while mitigating damage efficiently. Finally, we applied optimized conditions to investigate a perovskite compound using X-ray ptychography, reaching a 14-nm spatial resolution, an outcome that has never been attained so far.

1. Introduction

Metal halide perovskite (MHP) materials have received enormous attention due to their photovoltaic and optoelectronic properties suitable for solar cells,1,2 photonic devices,3,4 and X-ray detectors.5 However, many aspects of their properties must be...
uncovered to move their technologies from lab to market.\cite{6} The MHP instabilities under operation and the correlated photo-structural-chemical transformations require advanced characterization tools coupled with in situ and operando experiments for a comprehensive nanoscale view.\cite{7} Focused beam X-ray fluorescence (XRF),\cite{8} X-ray diffraction (XRD),\cite{9,10} X-ray beam-induced current (XBIC),\cite{11} X-ray excited optical luminescence (XEOL)\cite{12} and coherent diffraction imaging (CDI)\cite{13} more and more sophisticated and accessible at fourth-generation synchrotron sources, are powerful tools to investigate MHPs, or even complete perovskite solar cells (PSCs). Nevertheless, in most cases, those tools strongly interact with the materials leading to undesirable transformations. Although promising, focused X-ray-based techniques face high radiation doses deposited on the samples, which may cause damage to the materials and devices, altering their properties. Stuckelberger et al.\cite{14} showed that the electronic properties of the perovskite are the most sensitive, leading to a drastic reduction of the XBIC signal under X-ray irradiation but with no evidence of the element’s composition changes. X-ray photoemission (XPS) experiments also demonstrated the sensibility of the electronic properties, suggesting that the organic part of the perovskite (formamidinium (FA) and methylammonium (MA)) suffer radiolysis, producing volatile species.\cite{15,16} Orri et al. revealed that the degradation mechanism for electrons and X-rays is similar and is probably caused by the interaction of electrons, also generated by the X-rays, with the organic part of the MHP. In defective grain boundaries, even low doses of electrons lead to changes in grain orientation.\cite{17} Also, the degradation seems to be facet dependent, indicating that the sample crystalline quality is crucial to the resilience to X-ray damage.\cite{18} Interestingly, the cryogenic conditions do not avoid degradation but favor sample amorphization.\cite{19,20} Conversely, temperatures around 90 °C do not induce additional severe perovskite degradation.\cite{19} Besides the critical insights already uncovered, a comprehensive investigation of all X-ray dose aspects on the morphological, structural, and chemical properties of the MHP films extensively applied in PSC devices is still missing.

In this work, we use a correlative multi-technique approach to investigate the effect of the focused X-ray beam on the element’s distribution, morphology, structure, and optoelectronic properties of the [(FA\text{PbI}_3)_{0.87}(\text{MAPbBr}_3)_{0.13}]_{0.92}(\text{CsPbI}_3)_{0.08}(\text{CsFAMAPb(Br,I)_3}) compound. Such composition is relevant because it is widely used in fundamental studies and devices and presents a mixture of the main elements/molecules used in MHP. We irradiated the samples with controlled X-ray doses under different atmospheres and temperatures and evaluated the damage using correlative multiple micro and nanoscale techniques. The correlative data showed that the X-ray dose caused damage on the exposed surface, mainly affecting the iodine and organic elemental components, leading to topographical changes by yanking material out and forming an excavated area. The local optical properties within this area indicate the formation of a metallic layer coating the surface. Surprisingly, the bulk material under more severe doses preserved its optoelectronic properties. As expected, decreasing the X-ray dose, and using an inert atmosphere, reduced the damage. However, selective yanking out seems to be independent of the temperature conditions. We demonstrate that combining an inert atmosphere with a controlled dose reduction at room temperature is the way to proceed for investigating hybrid organic-inorganic MPHs with state-of-the-art X-ray nanoprobes. Finally, we applied the optimized conditions below the critical dose to demonstrate the feasibility of studying MHPs with the X-ray ptychography (CDI) technique and
highlighted the grain morphology and sample details with a 14-nm spatial resolution. Such a technique had never been reported before in these compounds.

2. Results and discussion

We deposited the perovskite CsFAMAPb(Br,I)\textsubscript{3} using the traditional antisolvent method onto Si/Au substrates (see details in the experimental section). This substrate is well-suited for this study because it allows X-ray and other correlative characterization techniques, such as Fourier-transform infrared micro-spectroscopy (\(\mu\text{-FTIR}\)), atomic force microscopy (AFM) and micro-photoluminescence (\(\mu\text{-PL}\)). The X-ray beam damage was investigated at the CARNÁÚBA X-ray Nanoprobe beamline of the LNLS/CNPEM.\textsuperscript{[21]} The Sirius storage ring was running at 3 GeV and 100 mA,\textsuperscript{[22]} with the beamline delivering a nanobeam of 200 nm (V)x500 nm (H) and a photon flux of \(5 \times 10^9\) ph/s at 10 keV. The methodology to get information on damage consisted of irradiating a small portion of the sample (5x5 \(\mu\text{m}^2\)) with controlled X-ray doses and environmental conditions, then mapping the previously irradiated area employing controlled doses over a larger area (10x10 \(\mu\text{m}^2\)). Fiducial marks on the samples allow them to move to other instruments to perform correlative measurements.

Figure 1\textsuperscript{a} shows a 5x5 \(\mu\text{m}^2\) nano-XRF map of the iodine acquired at room temperature and in an air atmosphere (RT-Air). To irradiate and map the sample, we used the fly-scan snake mode with the scan starting on the left-bottom corner of the image and the beam spot going up and down while sliding to the right related to the sample. The X-ray dose after irradiation corresponds to about 2.9 G Gy deposited in the scanned region, where 1 Gy = 1 J/kg is a measure of the total energy deposited per quantity of material irradiated.\textsuperscript{[23,24]} The estimated dose considers the compound’s total absorption at the irradiation energy so that doses deposited using different X-ray energies can be appropriately compared. The total amount of absorbed 10 keV photons by the 330-nm-thick perovskite film corresponds to \(2.53 \times 10^{21}\) ph/m\(^2\). We present the dose calculation and its Python code in the SI.

A noticeable effect in Figure 1\textsuperscript{a} is the decreasing iodine fluorescence emission in the scan direction from left to right. This gradient is not fortuitous but is systematically observed in different samples under similar doses (Figure S2). It can be understood as a yanking out caused by the X-ray beam on the surface that consumes an amount of iodine. As the horizontal nanoprobe (500 nm in size) is larger than the fly-scan step (200 nm), the initial irradiation (first vertical lines) hits a fresh sample. In contrast, the following vertical lines have already seen the beam and lost some material. The iodine consumption in the irradiated region is better observed in Figure 1\textsuperscript{b}. To inspect the irradiated region, we performed a larger scan of 10x10 \(\mu\text{m}^2\) centered at the same point as for the 5x5 \(\mu\text{m}^2\) one but with a much lower dose, corresponding to about 0.2 G Gy in the whole scanned region, which represents about 7\% of the dose in the former scan. The iodine map reveals a reduction of the number of iodine atoms in a square with the exact dimension of the previously irradiated region. The average fluorescence counts correspond to about a 28\% decrease. Interestingly, the Pb and Br maps do not show any evidence of composition changes (Figure 1\textsuperscript{c-d}).
As the hybrid organic-inorganic perovskite is composed of a mixture of MA and FA, which are not observable by XRF, the effect on the organic part was evaluated using µ-FTIR. Figure 1e shows a µ-FTIR map obtained by the integration of the C-N antisymmetric stretching vibration (1700 cm$^{-1}$) of the FA molecules. The decreased intensity in the X-ray irradiated region indicates that the FA molecules are also removed or degraded in the same area as for iodine. Comparing the complete FTIR spectra in the inner damaged region with the outer part (reference) reveals a change in the background for higher wavenumber (Figure 1f), which indicate a compound with a more metallic characteristic and different refraction index on the sample surface. This hypothesis is also qualitatively corroborated by a different color observed in the optical microscopy image shown in Figure 1i. The AFM measurements revealed the effect of the beam on the film topography (Figure 1g). We observed a film depth in the irradiated area corroborating...
with the material consumption already observed for iodine and organic molecules. Besides the depth, the grain size and shape inside the excavation look like the non-irradiated part without noticeable morphological changes. We expected that the decrease in iodine and organic cations content would affect the optic-electronic properties measured by μ-PL. However, the PL peak in the irradiated region remains stable in shape and position, with decreased intensity. Figure 1h, showing the PL spectra acquired using a μ-PL instrument with a spot size of 1 μm, indicates that the remaining perovskite compound preserves the bandgap properties.

Controlling Dose effects

The total X-ray dose effect was first investigated at room temperature and air atmosphere (RT-Air) conditions with a fixed photon flux yielding an absorbed dose rate of 4.7 KGY/s at a film area of 5x5 μm². The irradiation time was adapted so that the samples absorbed three different dose levels: 2.9 GGY (previous results in Figure 1), 1.9 GGY, and 0.7 GGY. As mentioned above, the 10x10 μm² inspection corresponds to 0.2 GGY. The corresponding number of 10 keV photons is given in Table S1. The data set in Figure 2a is the same as in Figure 1 but is represented again along with the two new sets with medium and low doses (Figure 2b-c) for comparison.

The 1.9 GGY and 0.7 GGY dose levels (Figures 2b and 2c, respectively) attenuate the iodine consumption, with a decreasing effect as the total deposited dose is reduced. Comparing the ratio between the iodine fluorescence in a 1x1 μm² area in the inner and the non-irradiated regions, we note that the highest dose leads to an iodine consumption of about 28%, reduced to 16% at 1.9 GGY and to 5% at 0.7 GGY (Figure 2d).

Regarding the organic cations, the μ-FTIR map (Figure 2a-c, FTIR column) shows the expected tendency of diminishing the beam damage with the smaller amount of energy deposited on the sample, with the effect mitigation with the beam attenuation by a factor of 4 (0.7 GGY dose). The tendency is clear by evaluating the integrated profile at the 1700 cm⁻¹ resonance (C-N antisymmetric stretching) in the irradiated region, which gives about a 30% decrease for the two highest doses and is absent for the smallest one (Figure 2e). The profile shows an intensity reduction broader than the irradiated area (pink column), which should come partially from the limited spatial resolution at 1700 cm⁻¹ due to the diffraction limit at this wavelength (5882 nm). This effect reduces at shorter wavelengths, as shown by the μ-FTIR images at the region of N-H stretching vibrations (3100-3400 cm⁻¹) (Figure S3), with a sharper profile more consistent with the irradiated area.

The iodine decrease in the irradiated region and the reduction of the signal from FA corroborates with the excavation in the irradiated area. The total thickness of the perovskite was measured by a profilometer to be 330 nm and compared to the depth observed in the AFM topographic images (Figure 2f). The total depth and ratio of the excavation in relation to the entire film thickness are estimated to be 90 nm (27%), 70 nm (21%), and 15 nm (5%) from the highest to smallest dose, respectively. These ratios are comparable to the iodine attenuation shown in Figure 2d. We should point out that error bars for these measurements are within 15%, as measured by the statistical fluctuations
outside the irradiated area. Interestingly, from the highest to the lowest dose, we can see a color transition from a pinkish tonality to a dark greenish to an almost imperceptible light green (Figure S4). Such color changes can result from a combination of effects, as the change in the sample thickness and the formation of a thin metallic layer.

These experiments were performed using the same dose rate and changing the exposition time. One can inquire which parameter is relevant, dose rate or total dose. To verify if the damage depends on the dose rate, we measured the iodine fluorescence signal as a function of time at a fixed sample position for two different dose rates (1.2 and 0.23 GGy/s) at the energy of 10 keV. Figure 3a shows that the higher dose rate causes the expected faster decay in the iodine content. However, when we present the iodine consumption not as a function of time but as a function of the total absorbed dose (Figure

**Figure 2**: Absorbed dose effect in air atmosphere. From left to right, nano-XRF damage scan, nano-XRF probe scan, C-N antisymmetric streching μ-FTIR, AFM and optical images for doses of (a) 2.9 GGy, (b) 1.9 GGy, and (c) 0.7 GGy. (d) Attenuation in the iodine content, (e) μ-FTIR intensity and (f) AFM profiles for the different doses.
**Figure 3:** Effect of the absorbed dose rate on iodine signal with the X-ray beam in a fixed position for two different absorbed dose rates. (a) Normalized iodine XRF signal in function of (a) time and (b) the dose.

3b), we note that the iodine decays for both dose rates are superimposed. The decaying signal fits with two exponential components for both dose rates and gives similar decay coefficients: 972 and 28 GGY$^{-1}$ for 1.2 GGY/s; and 916 and 36 GGY$^{-1}$ for 0.23 GGY/s, suggesting that two main processes occur independently of the dose rate. The free surface excavation is faster at the beginning, but once a certain quantity of material is depleted and a thin coating layer is formed, the process slows down. This experiment also demonstrates that reducing the dose rate is ineffective in mitigating beam damage in the air. What matters is the integrated absorbed dose needed to extract reliable pieces of information from the X-ray techniques. For completeness, a similar experiment was performed at two different photon energies, 10 and 14 keV, below and above the Pb and Br absorption edges. The X-ray fluxes were controlled to achieve the same absorbed dose rate at both energies, accounting for absorption and photon energy variation. **Figure S5** shows that the variation in iodine content is the same for both X-ray energies as far as the absorbed dose is the same, corroborating the observation that the total dose absorbed by the material is the determining control factor to the iodine consumption in air and at room temperature.

**Controlling Environmental effects**

The atmosphere and temperature conditions were investigated as another strategy to mitigate the beam damage. The same dose conditions (2.9, 1.9, and 0.7 GGY) were applied in three different environmental conditions: room temperature and air atmosphere (RT-Air), RT and nitrogen flow (RT-N$_2$), and cryogenic temperature (152K) and N$_2$ flow (Cryo-N$_2$). The RT-Air condition corresponds to the measurements discussed previously (**Figure 1** and **Figure 2**). At the 2.9 GGY and RT-N$_2$ conditions, a faint irradiated area (with no lateral gradient) was observed (**Figure 4a**, XRF columns), yielding an iodine quantity reduced by about 16% (**Figure 4c**), which is less compared to the same dose and RT-Air conditions (**Figure 2**). The Cryo-N$_2$ condition (**Figure 4b**, XRF columns) seems to mitigate the effect in the XRF maps, with no observable inorganic yanking out in the scanned region within the error bar of ±15%. The Cryo-N$_2$ condition seems to freeze the iodine mobility. Surprisingly, the damage persists in the organic part for both RT-N$_2$ and Cryo-N$_2$ (**Figure 4a-b**, μ-FTIR column), with similar intensity (**Figure 4d**). The AFM topography (**Figure 4a-b**, AFM column) confirms that the inert atmosphere does not
entirely mitigate the beam excavation. An additional effect observed in the Cryo-N₂ condition is the formation of cracks in the irradiated region, probably caused by the decreased ionic mobility that tends to relax some stress. Lastly, the optical inspection (Figure S6) shows that the irradiated regions changed color as previously. However, none presented the intermediate dark greenish, as before. Both inert atmosphere conditions showed a soft light greenish, like in the lowest dose of 0.7 GGY in air. This observation is essential once it indicates that the color change is, at least, not exclusively related to the thin film thickness variation and probably depends on the layer compound formed on the surface.

The intense X-ray dose on hybrid organic-inorganic MHP produces an ion-selective yanking out at the film surface, consuming iodine and organic cations but leaving Pb and Br composition unaltered, causing an excavation and altering the visible optical surface properties. As expected, the X-ray dose limitation reduces damage with almost complete mitigation of the iodine and organic molecules consumption. Under a similar dose but N₂ atmosphere, all damage effects reduce, suggesting that the inert atmosphere is relevant to mitigating iodine yanking out from the sample and that the air (O₂ and H₂O) is somehow

**Figure 4** Effect temperature and atmosphere on damage. From left to right, nano-XRF damage scan, nano-XRF probe scan, μ-FTIR, AFM and optical images for samples measured at (a) room temperature and air, (b) room temperature and nitrogen and (c) cryogenic temperature and nitrogen. (d) Attenuation in the iodine content, (e) μ-FTIR intensity and (f) AFM depth profiles for the different conditions.

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active in the iodine remotion. The effectiveness of the N$_2$ atmosphere in mitigating damage has already been reported in these compounds.\textsuperscript{[26]} Nevertheless, even in an inert atmosphere, there is still damage under the 2.9 GGY dose, and such a critical dose should be avoided when investigating these compounds.

Figure 5: Perovskite damage with reduce dose and inert atmosphere. Sample irradiated with (a) 1.9 GGY and (b) 0.7 GGY in RT-N$_2$. From left to right, nano-XRF damage scan, nano-XRF probe scan and $\mu$-FTIR (1700 cm$^{-1}$). (c and d) Respective $\mu$-PL at RT-N$_2$ and Cryo-N$_2$.

Figure 5 shows the nano-XRF and $\mu$-FTIR of the regions measured with the two smaller doses, 1.9 and 0.7 GGY, at RT-N$_2$. Reducing the absorbed dose and combining it with an inert atmosphere effectively reduce the damage. The inorganic elemental distribution is stable, even if the organic component still suffers a reduction. The topographic look-up by AFM (not shown) did not present any observable excavation. Interestingly, the photoluminescence properties are almost unaltered at the RT-N$_2$ condition, with a slight blueshift emission compared to the pristine sample (Figure 5c-d, column $\mu$-PL). We show, in addition, the Cryo-N$_2$ condition to demonstrate that the compound is more affected, as far as the photonic properties are concerned, at cryogenic temperatures. We observe a more significant shift and a broadening in the emission. Surprisingly, the lowest dose yields the largest shift and broadening.

Our results bring fundamental insights into the damage caused by intensely focused X-ray beams on perovskite compound. Figure 6 shows a schematic view of the damage caused by the X-ray beam in the MHP. The X-ray absorption cross-section of the light elements, such as carbon and nitrogen from the organic part of the perovskite, is very weak, and the organic molecules are essentially transparent to the X-ray beam. On the contrary, the inorganic cage of heavy atoms absorbs the X-ray photons more efficiently, decaying through different pathways, including the emission of electrons that interact more effectively with the organic molecules, eventually creating ions or radicals. Both are reactive and can be neutralized or undergo reactions with another species.\textsuperscript{[27,28]} Several
different reactions can be proposed between the ions and radicals with defects in the perovskite compound. These reactions produce new species that can be trapped in the structure or released as a gas, for instance, PbBr$_2$ crystallite or I$_2$ molecule. This process will create new punctual defects in the compound, eventually modifying their properties. But if several defects are formed near each other, the 3D perovskite cage will be destroyed. Therefore, a small or intermediate dose could produce a defective material compared to a destroyed one by a severe dose.

The conservation of energy and momentum dictates that the electron must transfer energy to an atom when they interact in elastic scattering. If the transferred energy exceeds the displacement energy ($E_d$), the atom moves to an interstitial position creating a defect. The $E_d$ depends on the atom’s bond strength, crystal lattice, and atomic weight.[29] As the perovskite is composed of medium to heavy elements, an intense displacement in the bulk is not expected. However, if an atom is at the surface, the $E_d$ is lower, and the atom can leave the specimen in a sputtering-like process.[29] One expects a high sputtering contribution from the organic molecules, independently of the atmosphere and temperature. However, those from the inorganic elements (Pb, I, and Br) should be smaller unless they have high mobility and are more reactive, as is the case of the iodine ions exposed to the air atmosphere.

Hence, the MHP damage mechanism combines radiolysis and sputtering. The radiolysis produces reactive species that react with other elements leading to the formation of volatile species that leave the sample. In the air, the O$_2$ and H$_2$O molecules can react with perovskite in different ways forming solid species such as PbO, Pb(OH)$_2$, PbCO$_3$, PbOH, Pb, PbI$_2$, and PbBr$_2$. Orri et al. [32] reported forming the PbBr$_2$ crystalline phase as a product after electron or X-ray irradiation. Also, volatile species such as I$_2$, HI, and deprotonated or degraded FA/MA molecules ($\text{CH}_3\text{I}$, NH$_3$, HCN, $\text{C}_3\text{H}_3\text{N}_3$) can form and leave the sample.[33–35] The iodine departure is corroborated by the absence of iodine accumulation at the boundaries of the 5x5 $\mu$m$^2$ irradiated area. These reactions probably occur more on the surface where the sputtering is more intense, and volatile molecules face a short path to escape. The N$_2$ atmosphere inhibits the O$_2$ and H$_2$O degradation paths. Consequently, the degradation is less severe, and inhibiting the formation of the iodine volatile species limits the iodine yanking out. However, the organic molecules still suffer from radiolysis and sputtering.
Nanoimaging by X-ray ptychography

To highlight the relevance of controlling the X-ray dose and environmental conditions when applying X-ray nanoscopy for perovskite investigation, we report an X-ray ptychography study in an MHP compound. X-ray ptychography \cite{13} is a phase contrast technique that reveals morphological aspects not seen in traditional scanning X-ray microscopy in transmission (STXM) or fluorescence (SXFM) modes. As a phase contrast technique, it is more sensitive to low-Z elements than absorption contrast techniques. We prepared and intentionally irradiated a Cs$_{0.05}$FA$_{0.95}$PbI$_3$ perovskite film, depositing a severe dose of 350 GGy on a single spot of 200x500 nm$^2$, corresponding to about $3.1 \times 10^{23}$ 10-keV-photons/m$^2$. After irradiation, we performed a ptychography map on a 10x10 $\mu$m$^2$ surface with steps of 100 nm, depositing a smaller dose of 0.0015 GGy.

Figure 7a shows the ptychography phase analysis, reaching a resolution close to 15 nm, which reveals the heterogeneous morphology and the damaged region bigger than 2 $\mu$m. The SXFM map (integrated over iodine and cesium fluorescence emissions) collected simultaneously (Figure 7b) reveals less resolved details owing both to the poorer statistics and worse spatial resolution. The inorganic damage around the same region shows up over a smaller area. The intentional irradiation removed some iodine over an area of about 1 $\mu$m$^2$ but depleted the organic molecules (seen by ptychography) over a larger area than the spot size. The STXM map did not show any contrast as expected. The possibility of measuring in fly-scan mode and under a controlled dose and N$_2$ atmosphere was essential to mitigate eventual sample damages. Clearly, the phase contrast brings new insights into the morphology and local heterogeneities of MHP compounds. Our multispectral images are a pivotal step in developing and applying the X-ray ptychography technique in beam-sensitive samples for high-resolution imaging, especially in the case of heterogeneous and hierarchical functional materials in which the multiscale properties determine final device performances.

![Figure 7](https://doi.org/10.26434/chemrxiv-2023-4w2wn)

**Figure 7**: Simultaneous X-ray ptychography and fluorescence images of a perovskite. (a) Ptychography, (b) overlayer of ptychography and (c) iodine nano-XRF images of Cs$_{0.05}$FA$_{0.95}$PbI$_3$ perovskite compound.
3. Conclusion

We applied a correlative multi-technique approach to investigate the damage caused by highly intense focused X-ray beams on hybrid organic-inorganic metal halide perovskites. Using focused X-ray beams for perovskite characterization will be challenging as the absorbed dose determines the damage, and each technique requires different doses to produce enough signal-to-noise ratio to extract information. Then, evaluating how the beam damage affects the desired properties is highly recommended before any material investigation. Our results show that combining an inert atmosphere with a reduced dose is compulsory to mitigate beam damage and provide conditions to understand the photo-structural-chemical dynamics of MHPs. Moreover, reporting the absorbed dose, or X-ray deposited power on samples, will help the community find the best experimental conditions to work safely. As a clear demonstration of how powerful the use of sophisticated new techniques in synchrotron radiation facilities can be, we applied the optimized conditions below the harmful dose to demonstrate the feasibility of investigating MHPs with the X-ray ptychography technique, uncovering morphological details never seen before.

4. Experimental

Sample preparation: The CsFAMAPb(I,Br)_3 perovskite with composition [(FAPbI)_0.87(MAPbBr)_0.13]_0.92(CsPbI)_0.08 was deposited by the antisolvent method on polished Si substrates covered with 100 nm of Au. The substrates were cleaned with isopropanol and ultraviolet-ozone (UVO) treated for 30 min before the deposition. The perovskite solution was prepared using FAI (GreatCell Solar Materials), MABr (GreatCell Solar Materials), PbI_2 (TCI America), PbBr_2 (TCI America), and CsI (TCI America) with a concentration of 0.7 M. The powders were dissolved in a mixture of anhydrous N, N-dimethylformamide (DMF, Sigma-Aldrich), and dimethyl sulfoxide (DMSO, Sigma-Aldrich) with a volume ratio of DMF:DMSO = 4:1 at room temperature. The solution was spin-coated at 2000 rpm for 12 s followed by 5000 rpm for 30 s. 15 s before the end of the spin-coating, 150 µL of chlorobenzene was dropped on the film. After deposition, the substrates were thermal annealed for 60 min at 100 °C. The Cs_{0.05}FA_{0.95}PbI_3 was deposited by the gas quenching method on the Mylar substrate.\(^{[36]}\) The substrates were cleaned with UVO treated for 30 min before deposition. The perovskite precursor solution was prepared by solubilizing CsI (TCI America), FAI (GreatCell Solar Materials), PbI_2 (TCI America) and 40 mol% of MACl, with an excess of 5% of the lead source, in the mixture of solvents DMF (Sigma-Aldrich) and methylpyrrolidone (NMP, Sigma-Aldrich) (v:v = 4:1) with a concentration of 1.3 M. The solution was spin-coated at 4000 rpm for 60 s. A jet of N_2 was automatically blown during the final 50 s of the rotation to force the solvent's exit and the perovskite's subsequent crystallization. The film was then heated at 100 °C for 90 minutes in the air.

Synchrotron experiments: For the same environment condition (RT-Air, RT-N_2 or Cryo-N_2), all X-ray measurements were performed in the same sample with a total size of ≈ 5x5 mm. Different areas spaced by 50 µm were measured, forming an array with different doses. The samples were positioned at the experimental station in front of the 500 x 200 nm² X-ray beam at the Tarumã Station at Carnaúba beamline.\(^{[21]}\) To obtain the nano-XRF, the X-ray beam irradiated the samples at the energies 10 and 14 keV and raster-scanned...
in a fly scan mode. For each position (x, y) was obtained an XRF spectrum. The nano-XRF maps were obtained using custom-made Python scripts integrating the XRF signals. The maps were obtained in the emissions I-Lα1 (3938 eV), Pb-Lα1 (10551 eV) and Br-Kα1 (11924 eV). Examples of the XRF spectrum for the 10 and 14 keV and corresponding peaks used to obtain the maps are shown in Figure S1. For the RT-N2 and Cryo-N2 experiments, the cryogenic sample environment was used. For the experiments with reduced doses, the phase of the undulator of the beamline was changed to reduce the X-ray flux. After the synchrotron experiments, the samples were stored in a vacuum and dry box until the other characterizations.

Three different X-ray fly scans were used to obtain the different doses in the same total area of 5x5 um. For 2.9 GGy, the step size was 100 nm, and exposure time of 750 ms by point. For 1.9 GGy, the step size was 60 nm with an exposure time of 58 ms. For 0.7 GGy the step size was 50 nm, and the exposure time of 8 ms. The irradiated areas were inspected with a 10x10 um scan, step size of 100 nm, and exposure time of 7.5 ms. More details about the scans can be found in Table S1.

The ratio of the iodine reduction was calculated by the average intensity of a 2x2 μm at the center of the irradiated area, a region does not irradiate with the same dimensions. The ratio presents an error of the ± 15% estimated from several images due to statistic fluctuation.

**Ptychography measurements**

The area of 10x10 μm² was scanned with a step of 100 nm, >50% overlap in the probe size (200x500) HxV nm², including random variations in the 10100 probe positions with respect to a perfect square grid to avoid raster artifacts in the reconstruction.[38] The scan was performed at the energy of 10 keV in fly-scan mode with a constant velocity of 10 μm/s with a total acquisition time of 172s. The total dose of this scan was estimated to be 0.0015 GGy.

For the reconstruction, 180 × 180 pixels (55x55 μm²) of the data PiMega area detector at the distance of 1.1 m from the sample were used, resulting in a pixel size of reconstruction of 13.7 nm. The object was initialized with random amplitude and phase maps. The probe was initialized with the inverse Fourier transform of the average of the diffraction patterns in the first mode. Six more modes were added as random fluctuations of the first mode, and their maximum intensities were normalized to 15% of the first mode. The reconstruction was performed by combining 100 iterations of the Alternating projections (AP)[39] algorithm, followed by 5000 iterations of the Relaxed averaged alternating reflections (RAAR)[40] method, and finally, 1000 iterations of AP. The final R factor of the reconstruction reached the value of 5.30%.[41,42]

μ-FTIR: The X-ray irradiated areas were identified by the optical microscopy coupled with the μ-FTIR equipment and then measured. The experiments were performed at the Infrared Micro and Nanospectroscopy (IMBUIA) beamline of the Brazilian Synchrotron Light Laboratory (LNLS) at the IMBUIA-Micro station. A blackbody infrared source in a commercial IR spectral microscope was used. The images were obtained using a focal plane array (FPA) IR detector with 256 scans, spectral resolution of 8 cm⁻¹. The μ-FTIR maps were obtained by custom-made Python scripts integrating the infrared signals.
**AFM:** The atomic force microscopy data were acquired at the In situ Growth Laboratory (LCIS) of the Brazilian Synchrotron Light Laboratory (LNLS), which is part of the Brazilian Center for Research in Energy and Materials (CNPEM). The images were obtained using a Nanosurf Flex AFM. Scans covered an area of 10x10 μm² with a step size of 20 nm at dynamic force contact mode with the cantilever type Tap 300-AI-G with 1.5 s per line. The data were analyzed with the Gwyddion software. The images in the paper correspond to the morphology acquired in the Z-axis forward direction. The Z-axis backward direction images were checked to exclude possible artifacts.

**μ-PL:** The μ-PL data were acquired at the Brazilian Nanotechnology National Laboratory (LNNano), which is part of the Brazilian Center for Research in Energy and Materials (CNPEM). The PL was obtained using a confocal Raman spectrometer Horiba Xplora plus. The damaged X-ray areas were found using optical microscopy coupled to the equipment, and then PL measurements were obtained in different regions with a beam size of around 1 μm. The excitation source was a 638 nm laser with a minimum power of 0.1% and a minimum integration time of 10 ms.

**Optical microscopy:** The optical microscopy images were acquired at the Laboratory of Microscopic Samples (LAM) of the Brazilian Synchrotron Light Laboratory (LNLS), which is part of the Brazilian Center for Research in Energy and Materials (CNPEM). The images were obtained using a Nikon Eclipse LV100-UDM-POL microscope with a magnification of 100x. The colors in the image represent the real colors of the surface.

**Supporting Information**
Supporting information is available.

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**Conflict of Interest**
The authors declare no conflict of interest.

**Keywords**
Metal halide perovskites, X-ray beam damage, perovskite solar cells, synchrotron radiation, X-ray nanoprobe.
References


