Supplementary information:

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

Francisco M. C. da Silva[1,2], Rodrigo Szostak[1], Maria G. D. Guaita[1,3], Verônica C. Teixeira[1], Ana F. Nogueira[3], Hélio C. N. Tolentino[1]

[1]Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, SP 13083-970, Brazil.

[2]University of Campinas (UNICAMP), Physics Institute (IFGW), Campinas, SP 13083-970, Brazil.

[3]University of Campinas (UNICAMP), Chemistry Institute (IQ), Laboratório de Nanotecnologia e Energia Solar (LNES), , Campinas, SP 13083-970, Brazil.

Correspondence to: Dr. Rodrigo Szostak, Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), Rua Giuseppe Máximo Solfaro, 10000, Campinas, SP 13083-100, Brazil. E-mail: rodrigo.szostak@lnls.br; Dr. Hélio Cesar Nogueira Tolentino, Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), Rua Giuseppe Máximo Solfaro, 10000, Campinas, SP 13083-100, Brazil. E-mail: helio.tolentino@lnls.br

Beam dose calculation

The X-ray dose was calculated by the total energy absorbed (J) by the sample mass (Kg). The unit 1 J/Kg equals 1 Gray (Gy), the SI unit of radiation dose.

The dose is calculated by the formula $D = \frac{NE}{m}$, where N is the number of absorbed photons, E is the photon energy, and m is the mass of the sample irradiated by the X-rays.

The N is calculated by the formula $N = \left(1 - e^{-du}\right) I_0 t$, where d is the sample thickness, μ is the X-ray attenuation length, I_0 is the total photon flux incident on the sample, and t is the exposition time. The mass m can be calculated by the formula $m = \rho A d$, where ρ is the sample density and A the X-ray irradiated area.

The dose can be calculated by the following Python code:

```python
#Libraries
from xraydb import material_mu  # Information about the xraydb library can be found at: https://xraypy.github.io/XrayDB/
from xraydb import atomic_mass
import numpy as np

#-------------------- Input parameters - Fill out your information ----------------------

# Perovskite composition - Fraction of elements/molecules by unit cell
Cs = 0.08
FA = 0.8
MA = 0.12
Pb = 1
Br = 0.37
I = 2.64

latt_par_a = 6.28 #Lattice parameter in Angstron (A)
latt_par_b = 6.28 #Lattice parameter in Angstron (A)
latt_par_c = 6.28 #Lattice parameter in Angstron (A)

I0 = 5.35e9             #X-ray photon flux in Photons/s
t = 410                 #Duration of the X-ray exposition in seconds (s)
Irradiated_area_H = 5e-6 #Horizontal dimension of the X-ray beam in meters(m)/Incidence direction
Irradiated_area_V = 5e-6 #Vertical dimension of the X-ray beam in meters(m)
Incidence_angle = 90     #Incidence angle in degrees (°)
E = 10000                #Energy of the X-ray beam  in eV
d = 330                  #Thickness of the perovskite layer in nanometers (nm)

# ----------------------------------Calculations--------------------------------------------------------

formula_1 = "Cs" + str(Cs) + "FA" + str(FA) + "MA" + str(MA) + "Pb" + str(Pb) + "I" + str(I) + "Br" + str(Br)
print("Perovskite formula: ", formula_1)

mass_sum_FA = atomic_mass("C")+ 5*atomic_mass("H")+ 2*atomic_mass("N")
mass_sum_MA = atomic_mass("C")+ 6*atomic_mass("H")+ atomic_mass("N")
mass_sum = Cs*atomic_mass("Cs") + FA*mass_sum_FA + MA*mass_sum_FA+ Pb*atomic_mass("Pb") + I*atomic_mass("I") + Br*atomic_mass("I")

cell_vol = (latt_par_a*latt_par_b*latt_par_c)*1e-30                         #Cell volume in m3
density = (mass_sum/(cell_vol*6.02214e23))/1e6                              #Density in g/cm3
A = Irradiated_area_H/np.sin(np.radians(Incidence_angle))*Irradiated_area_V   #Illuminated area considering footprint

# Fraction of organic atoms
C = round(FA+MA, 2)
N = round((2*FA)+MA, 2)
H = round((5*FA)+(6*MA), 2)

chemical_formula = "Cs" + str(Cs) + "C" + str(C) + "N" + str(N) + "H" + str(H) + "Pb" + str(Pb) + "I" + str(I) + "Br" + str(Br)
print("Elemental perovskite formula: ", chemical_formula)
print("Density: ", round(density,2) , "g/cm3")
mu = material_mu(chemical_formula , energy = E, density = density)   #X-ray attenuation length (in 1/cm) for a material

It = np.exp(-(d/1e7) * mu)                              #Transmitted photons
N = ((1-It)*I0)*t                                       #Number total of absorbed photons
D = ((N*E*1.6021e-19)/((density*1e3)*A*(d*1e-9)))       #Dose in Grays (Gy)

print("-----------------------------------------------------------")
print("Dose = ", '{:.2e}'.format(D), "Gy")
print("Total absorbed photons: ", '{:.2e}'.format(N))
print("Absorbed photons by area: ", '{:.2e}'.format(N/A), "Photons/m2")
print("Transmission: ", round(It,2), "%")
print("-----------------------------------------------------------")
```

```
Perovskite formula:  Cs0.08FA0.8MA0.12Pb1I2.64Br0.37
Elemental perovskite formula:  Cs0.08C0.92N1.72H4.72Pb1I2.64Br0.37
Density:  4.3 g/cm3
-----------------------------------------------------------
Dose =  1.90e+09 Gy
Total absorbed photons:  4.21e+10
Absorbed photons by area:  1.68e+21 Photons/m2
Transmission:  0.98 %
-----------------------------------------------------------
```

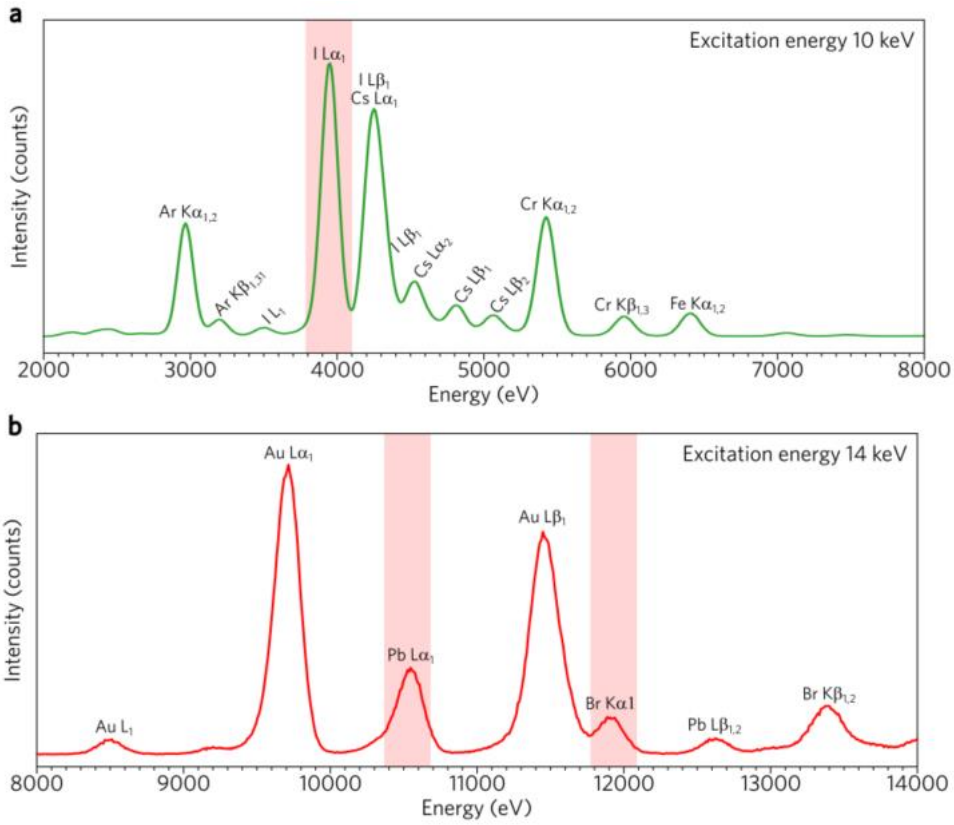

Figure S1: X-ray fluorescence spectrum obtained with X-ray excitation energy of (a) 10 keV and (b) 14 keV. The spectrum from each pixel was squeezed to obtain the spectrum shown here. The highlighted peak region was used to obtain the nano-XRF maps.

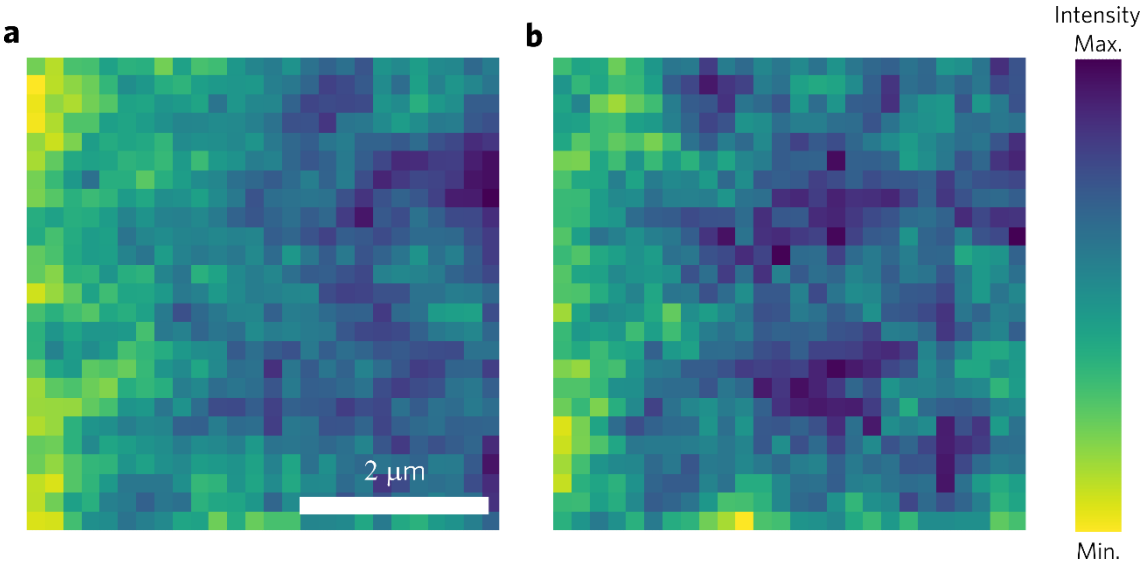

Figure S2: Iodine nano-XRF map obtained with the energy of 10 keV and total absorbed dose of 2.9 GGy in two different new regions of the sample.

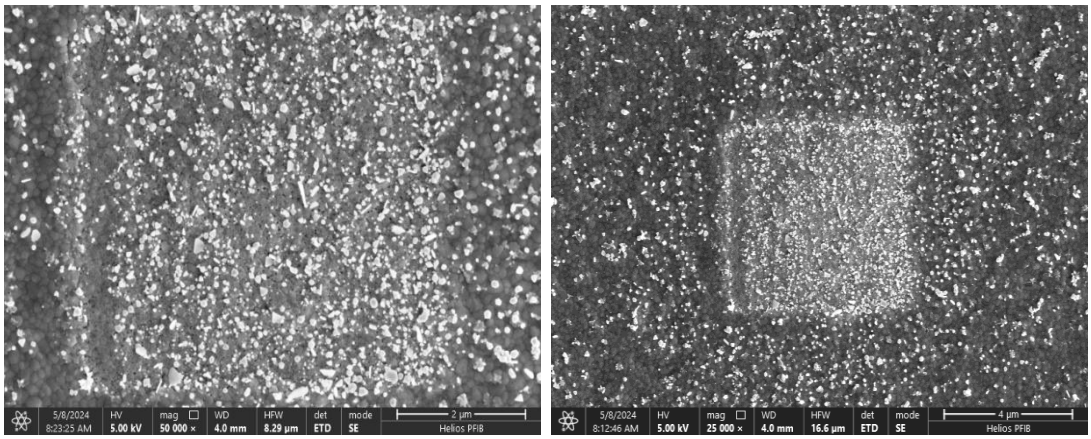

Figure S3: SEM images of the MHP irradiated in air showing the damaged area. This is not the same sample as in Figure 1, but it was prepared and irradiated under similar conditions.

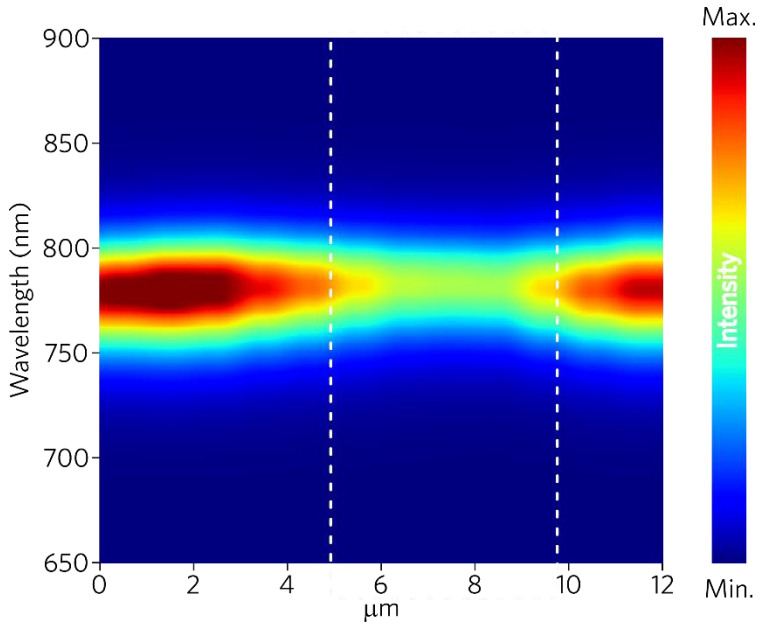

Figure S4: Photoluminescence line scan obtained through the damaged area of the sample irradiated with 2.9 GGy in air. The excitation was 638 nm with steps of 1 um.

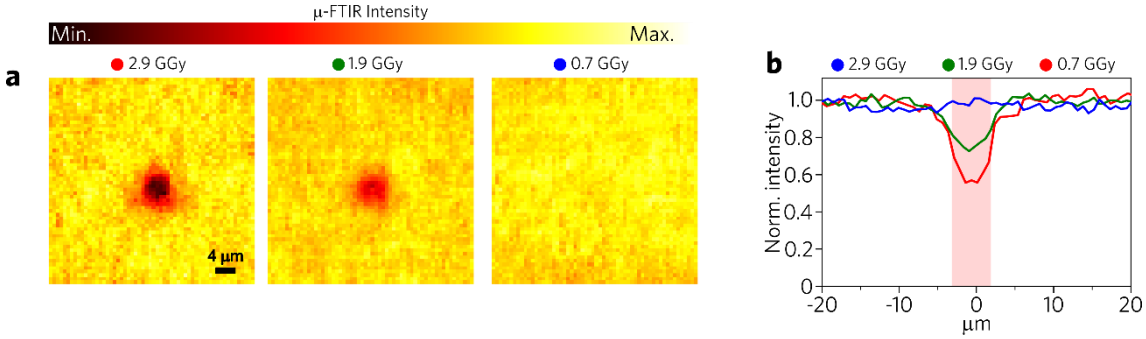

Figure S5: (a) μ-FTIR maps of the perovskite obtained integrating N-H stretch vibrations (3100-3400 cm^{-1}) for different X-ray beam doses in air, and (b) profile of the damaged area. Despite the smaller spatial resolution of the μ-FTIR at resonance 1700 cm^{-1} we chose this one for a more quantitative analysis because the changes in the background in this region are negligible. On the other side, the 3100-3400 cm^{-1} region shows a change in the background, then becomes difficult for a quantitative analysis using these resonances.

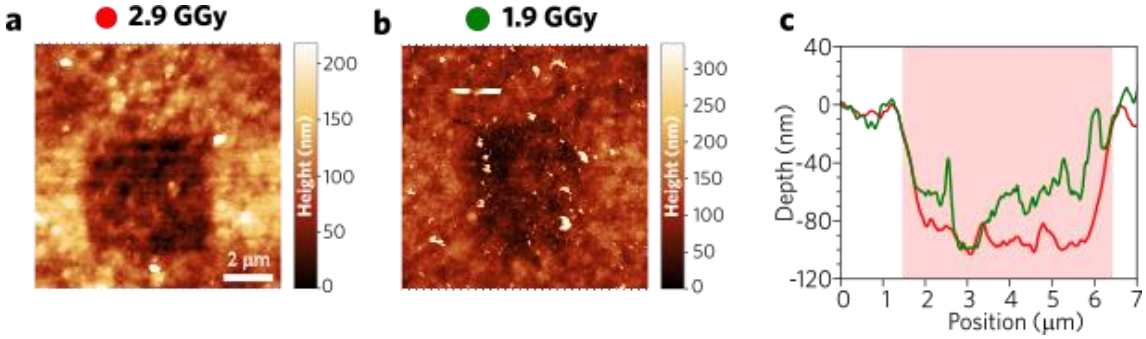

Figure S6: AFM images for doses of of (a) 2.9 GGy and (b) 1.9 GGy. (c) AFM profiles for the different doses. Note: In the sample irradiated with 0.7 GGy, it was not possible to find the damaged area on the AFM microscope.

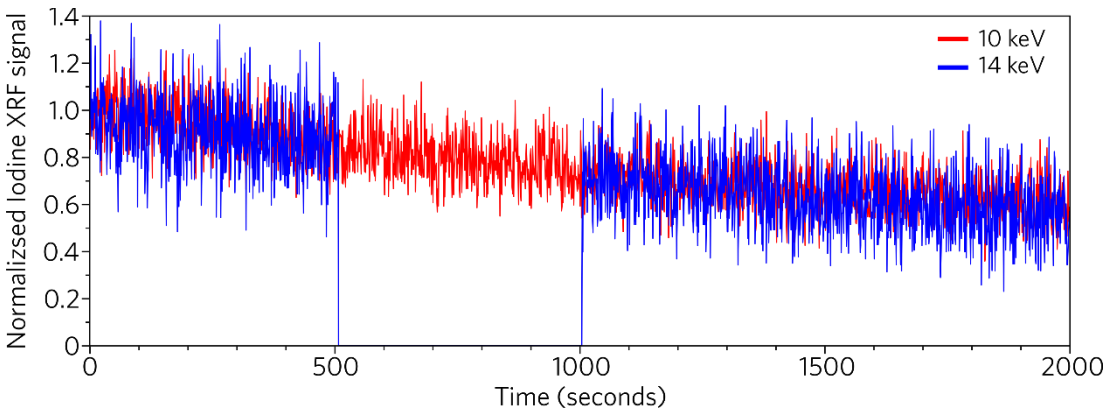

Figure S7: Effect of different X-ray beam energies with similar absorbed dose rates. The signal corresponds to the iodine XRF emission.

Table S1: Total absorbed photons for each dose

Energy (KeV)	Area (μm x μm)	Total time (s)	GGy	Total absorbed photons (x 10^{21} ph/m^2)
10	5 x 5	610	2.9	2.53
10	5 x 5	410	1.9	1.70
10	5 x 5	150	0.7	0.62
10	10 x 10	172	0.2	0.18
10	10 x 10	171	0.0015	0.0013
14	10 x 10	171	0.013	0.0084