

## *Supporting Information*

### **Releasing trapped excitons in 2D perovskites via pressure annealing: A cooperative interplay between lattice strain and electronic structure.**

Andre L. M. Freitas,<sup>a\*</sup> Naidel A. M. S. Caturello,<sup>b</sup> Aryane Tofanello,<sup>a</sup> Ulisses F. Kaneko,<sup>c,d</sup> Lucas E. Correa,<sup>c</sup> Ricardo D. dos Reis,<sup>c</sup> Fabio F. Ferreira,<sup>a</sup> Gustavo M. Dalpian<sup>e</sup> and Jose A. Souza<sup>a,\*</sup>

<sup>a</sup> Federal University of ABC (UFABC), CCNH, 09210-580, Santo André, SP – Brazil.

<sup>b</sup> Thomas Lord Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708, United States

<sup>c</sup> Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), 13083-970, Campinas, SP- Brazil

<sup>d</sup> São Paulo State University – UNESP, Institute of Geosciences and Exact Sciences (IGCE), Physics Department, Rio Claro, SP, Brazil

<sup>e</sup> Institute of Physics, University of São Paulo (USP), 05508-090, São Paulo, Brazil

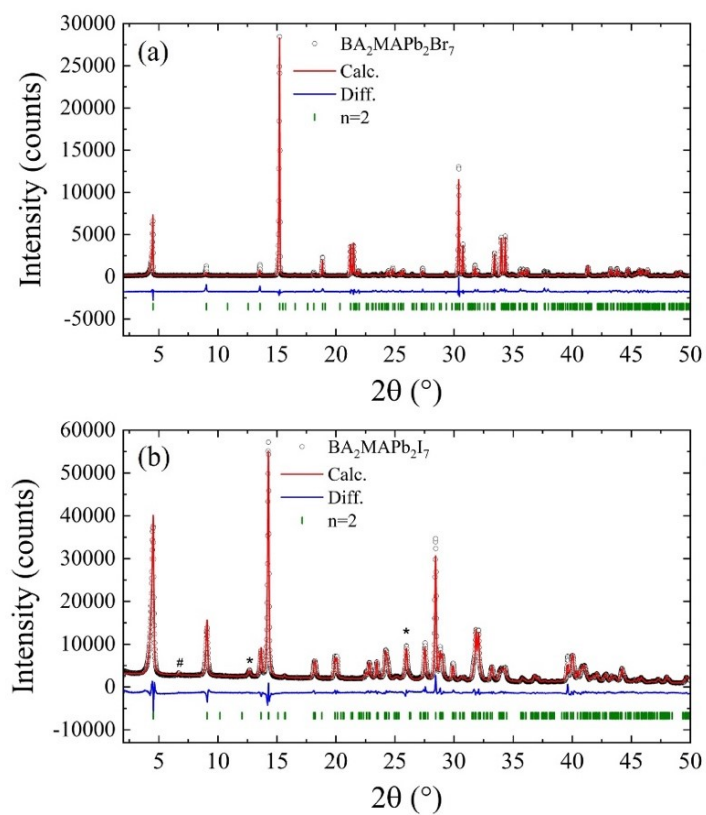
**Corresponding author:** andre\_luizmf@yahoo.com.br, joseantonio.souza@ufabc.edu.br

The Supporting Information contains the following:

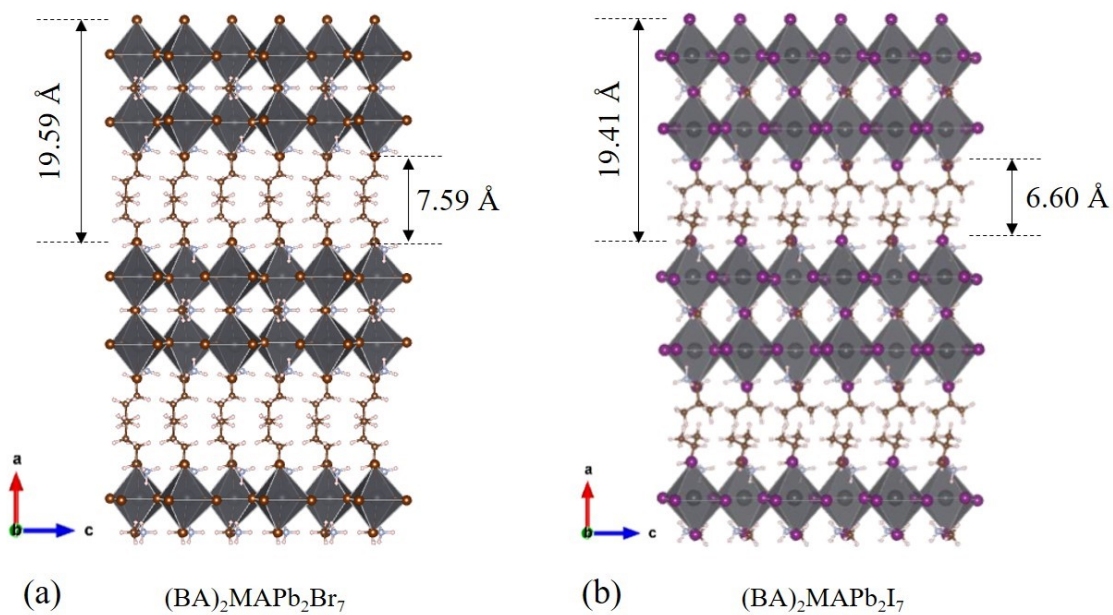
**Supplementary Note 1..... Further experimental results and their interpretation**

**Supplementary Note 2..... Further details of the RPP-type  $n = 2$  perovskite model**

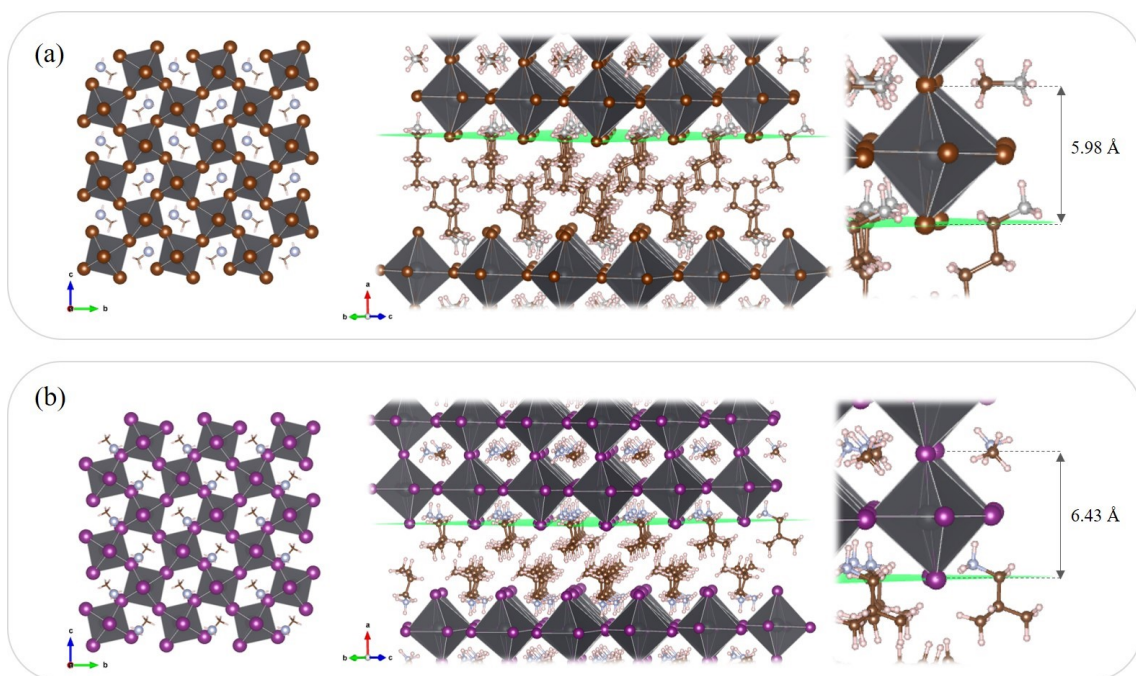
## Supplementary Note 1: Further experimental results and their interpretation



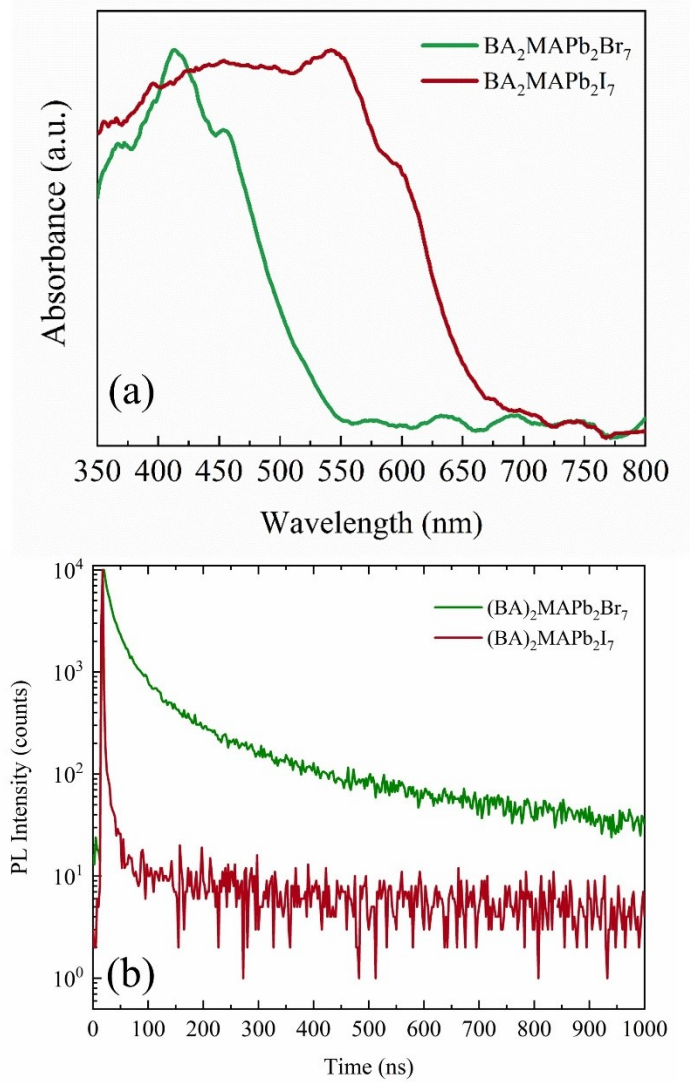
**Fig. S1.** XRD measurements along with Rietveld refinements for 2D-RP perovskites (a)  $\text{BA}_2\text{MAPb}_2\text{Br}_7$  and (b)  $\text{BA}_2\text{MAPb}_2\text{I}_7$ . Extra peaks were identified as additional phases (#)  $\text{BA}_2\text{PbI}_4$  and (\*)  $\text{PbI}_2$  with small concentration.



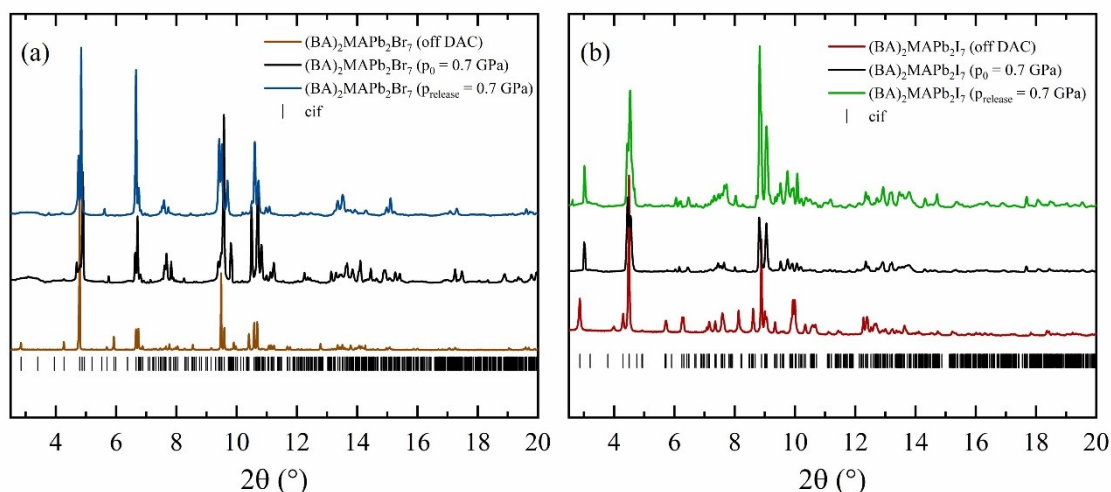
**Fig. S2.** Illustration depicting the interplanar distance and organic layer dimension along the a-axis stacking direction for (a)  $\text{BA}_2\text{MAPb}_2\text{Br}_7$  and (b)  $\text{BA}_2\text{MAPb}_2\text{I}_7$ .



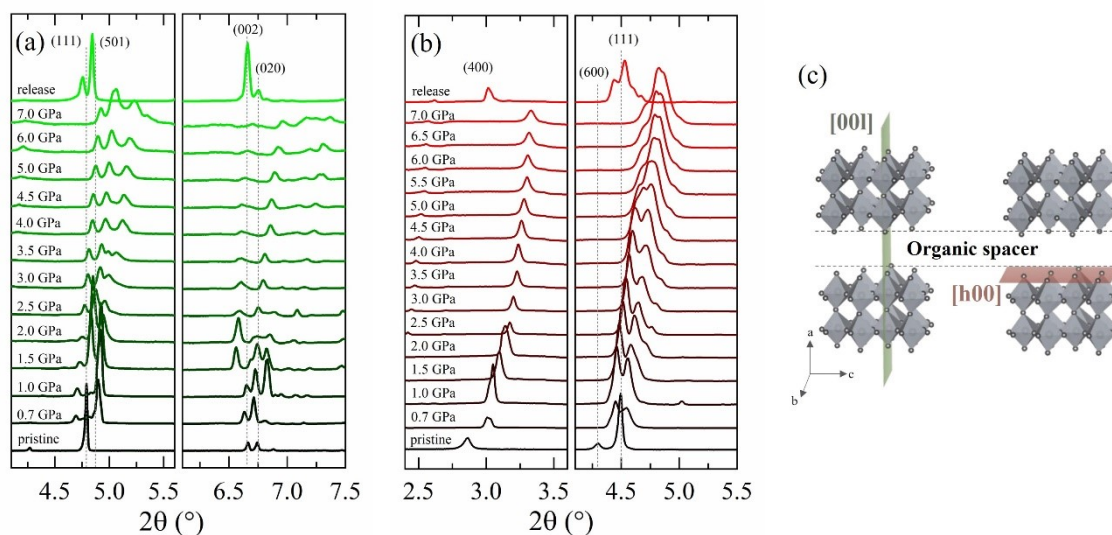
**Fig. S3.** Visualization of the *A*-site symmetry in the equatorial view and details of the organic spacer penetration into the halide plane defining the octahedron, highlighting the organic-inorganic interface for (a)  $\text{BA}_2\text{MAPb}_2\text{Br}_7$  and (b)  $\text{BA}_2\text{MAPb}_2\text{I}_7$ .



**Fig. S4.** (a) Steady-state absorption spectra and (b) time-resolved carrier lifetimes measured for uncompressed  $\text{BA}_2\text{MAPb}_2\text{Br}_7$  and  $\text{BA}_2\text{MAPb}_2\text{I}_7$ .

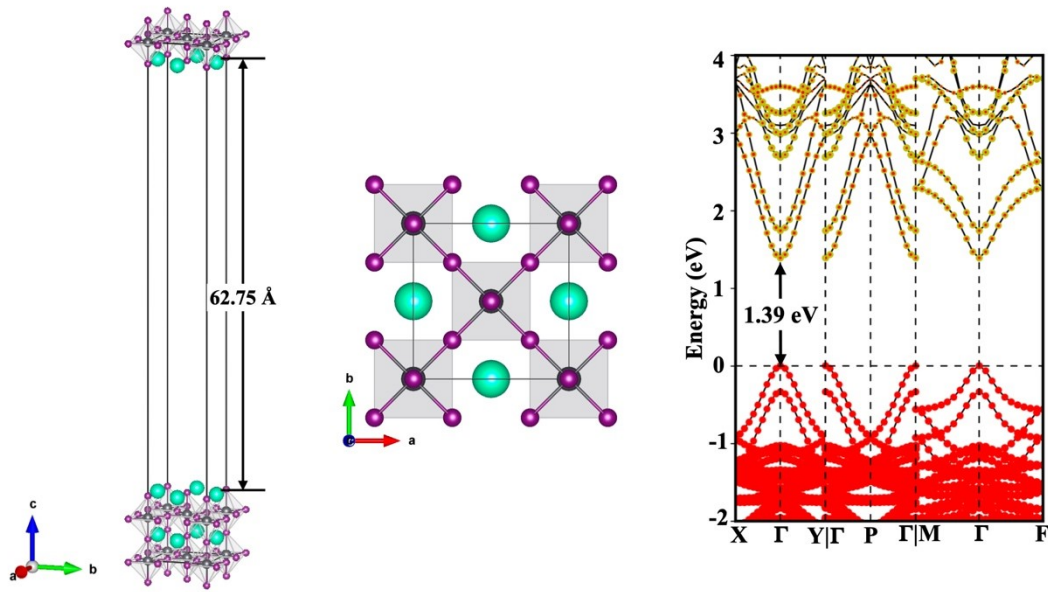


**Fig. S5.** In-situ synchrotron X-ray diffraction (XRD) patterns under applied pressure for three conditions: ambient conditions within the diamond anvil cell (DAC), low pressure (0.7 GPa), and post-release with residual pressure (0.7 GPa) for the samples (a)  $\text{BA}_2\text{MAPb}_2\text{Br}_7$  and (b)  $\text{BA}_2\text{MAPb}_2\text{I}_7$ .

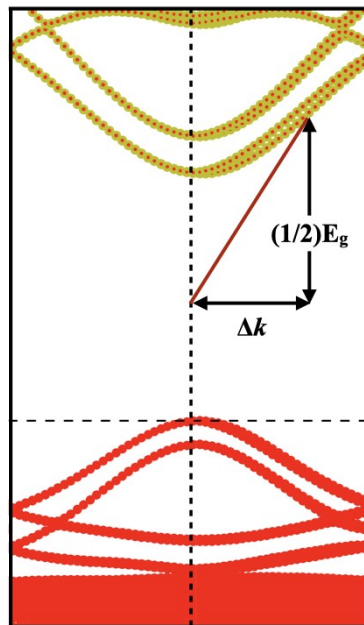


**Fig. S6.** Representative in-situ synchrotron XRD patterns for samples under applied pressure, (a)  $\text{BA}_2\text{MAPb}_2\text{Br}_7$  and (b)  $\text{BA}_2\text{MAPb}_2\text{I}_7$ . (c) Schematic representation of the crystallographic orientations in 2D ( $n=2$ ) perovskites:  $[001]$  directions are perpendicular, and  $[h00]$  directions are parallel to the layer stacking

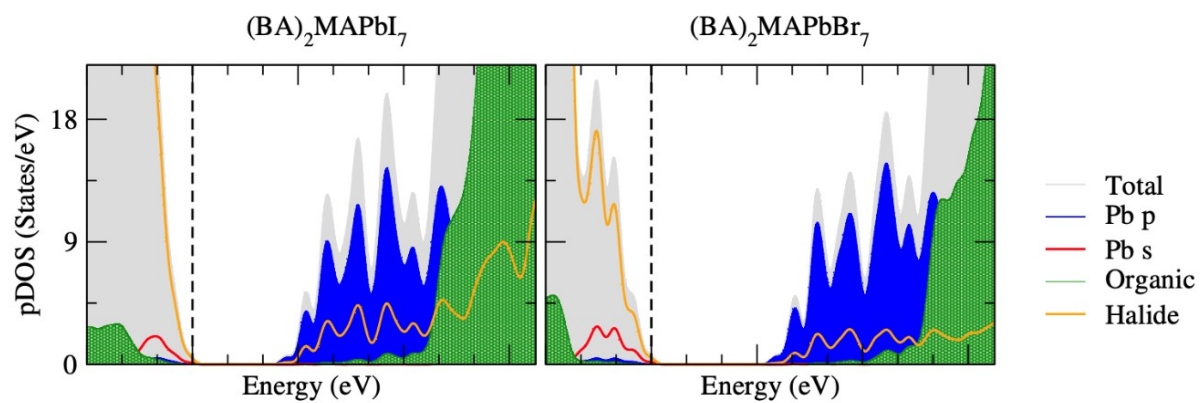
Supplementary Note 2: Further details of the RPP-type  $n = 2$  perovskite model



**Fig. S7.** Undistorted  $\text{Cs}_3\text{Pb}_2\text{I}_7$  RP-type,  $n = 2$  perovskite model and its species-decomposed HSE06+SOC band structure (red spheres are I; yellow spheres are Pb). We show the large interlayer distance ( $62.75 \text{ \AA}$ ) used to avoid interlayer interactions.



**Fig. S8.** The Kane energy defined according to Equation S16, represented schematically in a general band structure parabola. The slope is used according to the rationale of the Supplementary Note 4.



**Fig. S9.** HSE06+SOC projected density of states (pDOS) for the uncompressed RPPs.