Supporting Information for:

Mechanochemical Synthesis of Inorganic Halide Perovskites: Evolution of Phase-purity, Morphology, and Photoluminescence

Francisco Palazon,[a,b]* Yousra El Ajjouri,[a] Paz Sebastia-Luna,[a] Simone Lauciello,[c] Liberato Manna,[b] and Henk J. Bolink[a]

[a] Instituto de Ciencia Molecular, ICMol, Universidad de Valencia, C/ Catedrático J. Beltrán 2, 46980 Paterna, Spain

[b] Nanochemistry Department and [c] Electron Microscopy Facility, Istituto Italiano di Tecnologia (IIT), Genova, Italy

EXPERIMENTAL DETAILS

Materials

Cesium bromide (CsBr, > 99 %), was purchased from TCI. Lead(II) bromide ($PbBr_2$, ≥ 98 %) was purchased from Sigma-Aldrich. All chemicals were stored in a nitrogen-filled glovebox and used as received without further purification.

Mechanochemical Synthesis

Equimolar CsBr:$PbBr_2$ powders were mixed inside a nitrogen-filled glovebox. Then, approximately 3 grams of the mixed precursors powders was introduced inside 10 mL zirconia ball-mill jars with 2 zirconia beads of 10 mm in diameter. The jars were closed under nitrogen so that the powders were not exposed to air. Then ball-milling was performed with a MM-400 straight ball-mill from Retsch, at a frequency of 30 Hz for different times.

XRD characterization

X-ray diffraction was measured with a Panalytical Empyrean diffractometer equipped with CuKα anode operated at 45 kV and 30 mA and a Pixel 1D detector in scanning line mode. Single scans were acquired in the 2Θ = 10° to 90° range with a step size of 2Θ = 0.026º, in Bragg-Brentano geometry in air. For microstructural analysis, instrumental peak broadening was taken into account by measuring a reference silicon wafer under the same measurement conditions and refining the Thompson-Cox-Hastings pseudo-Voigt line shape parameters, used to create the instrument resolution file. All XRD analysis was carried out with Fullprof software. Whole-pattern Le Bail Fits are performed to refine cell parameters and line shape for microstructural analysis. Refined cell parameters are also used to carry out structural Rietveld refinement for quantitative analysis.

SEM / EDX characterization

Electron microscopy characterization (SEM and EDX) was performed using HRSEM JEOL JSM-7500L equipped with a cold field-emission gun (FEG) operating at 25 kV acceleration voltage and with an EDS Oxford instrument, X-Max, 80 mm^2.

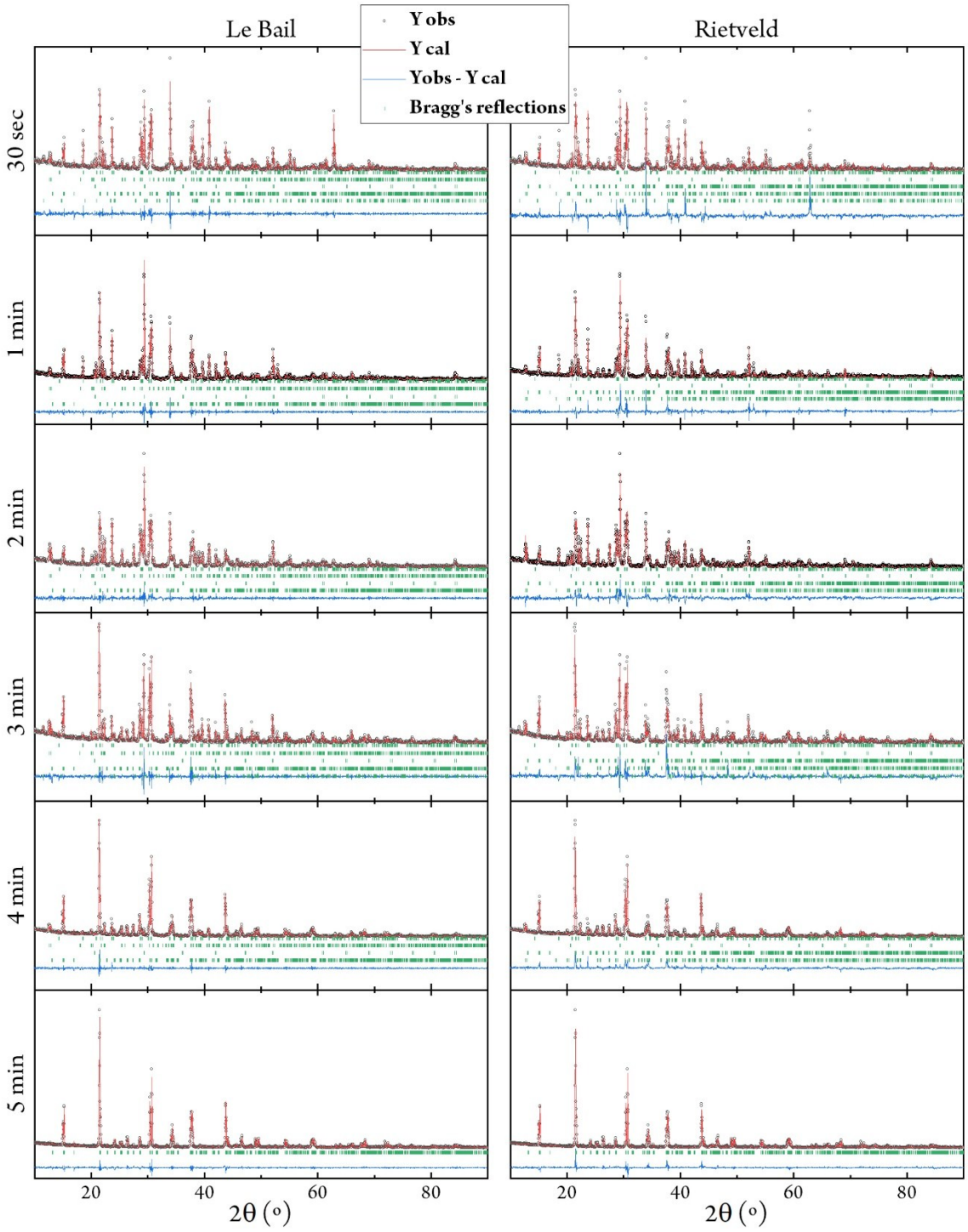

Figure S 1. Le Bail and Rietveld refinements of XRD data for samples ball-milled for 30 seconds, 1 minute, 2 minutes, 3minutes, 4 minutes, and 5 minutes.

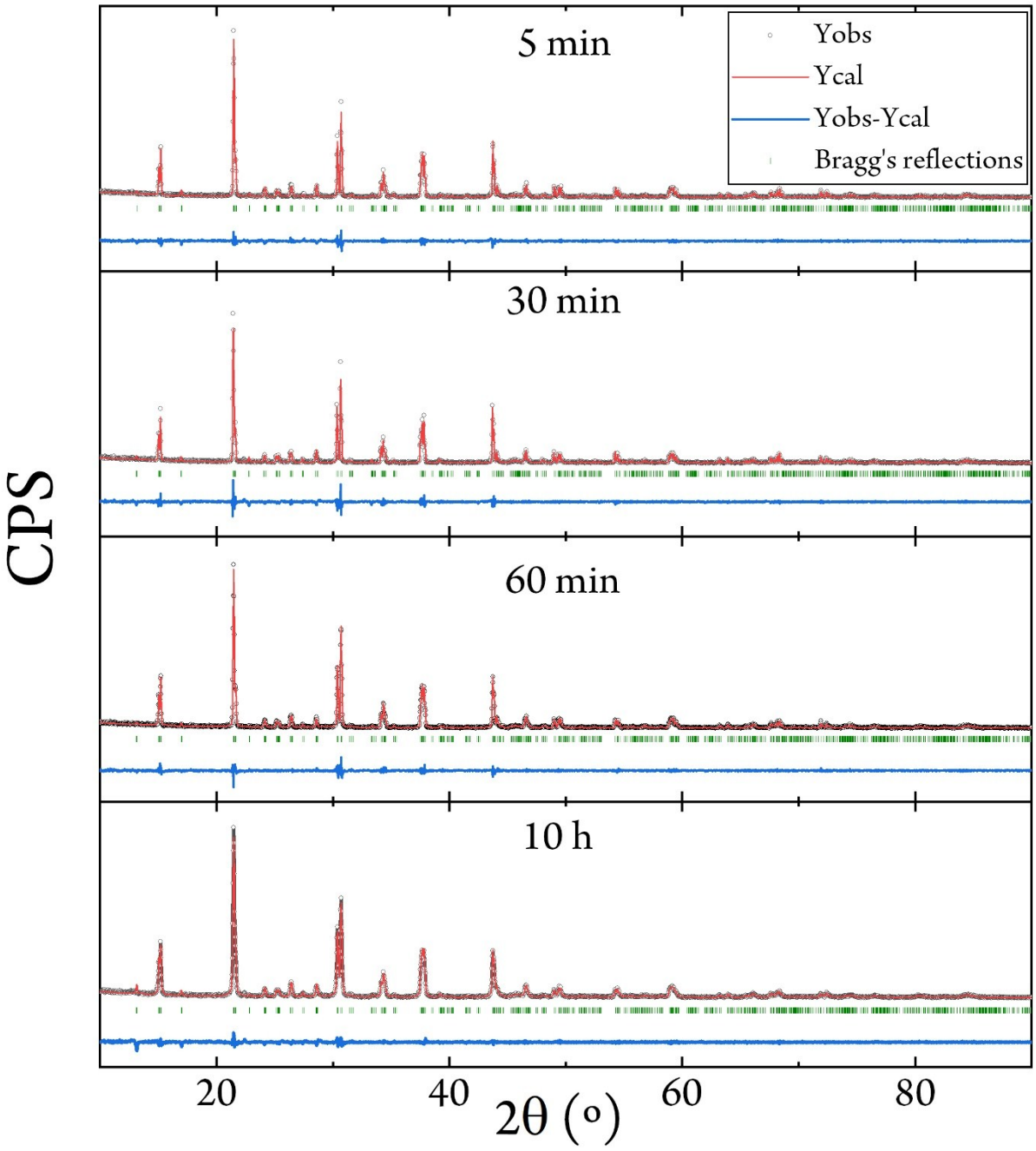

Figure S 2. XRD of samples ball-milled for 5 minutes, 30 minutes, 1 hour, and 10 hours, fitted with a single $CsPbBr_3$ phase.

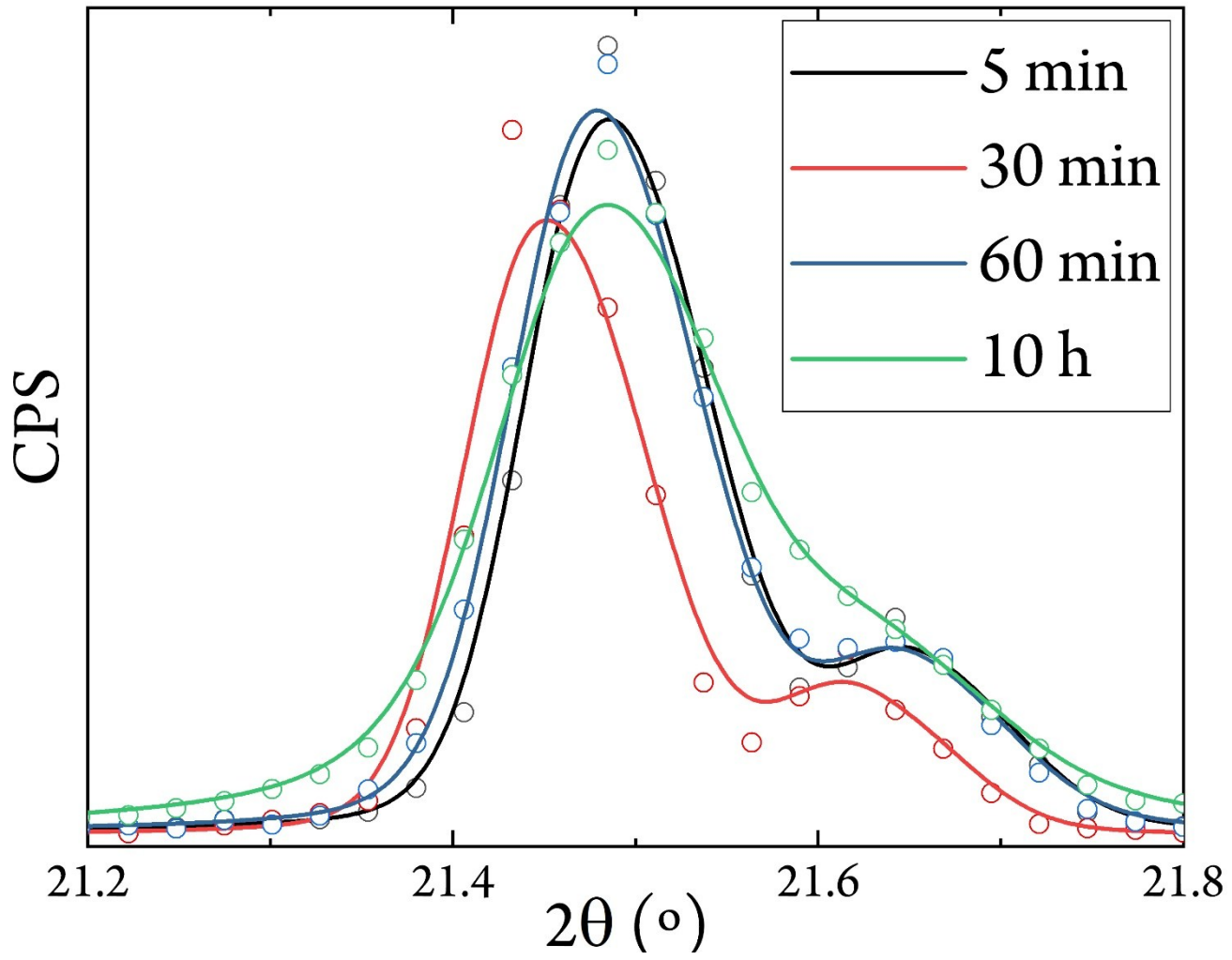

Figure S 3. XRD of main CsPbBr3 diffraction peaks showing broadening at long milling times (t = 10 h). A small shift of less than 0.05º is observed in one of the samples (t=30min) for which the reason is unclear.

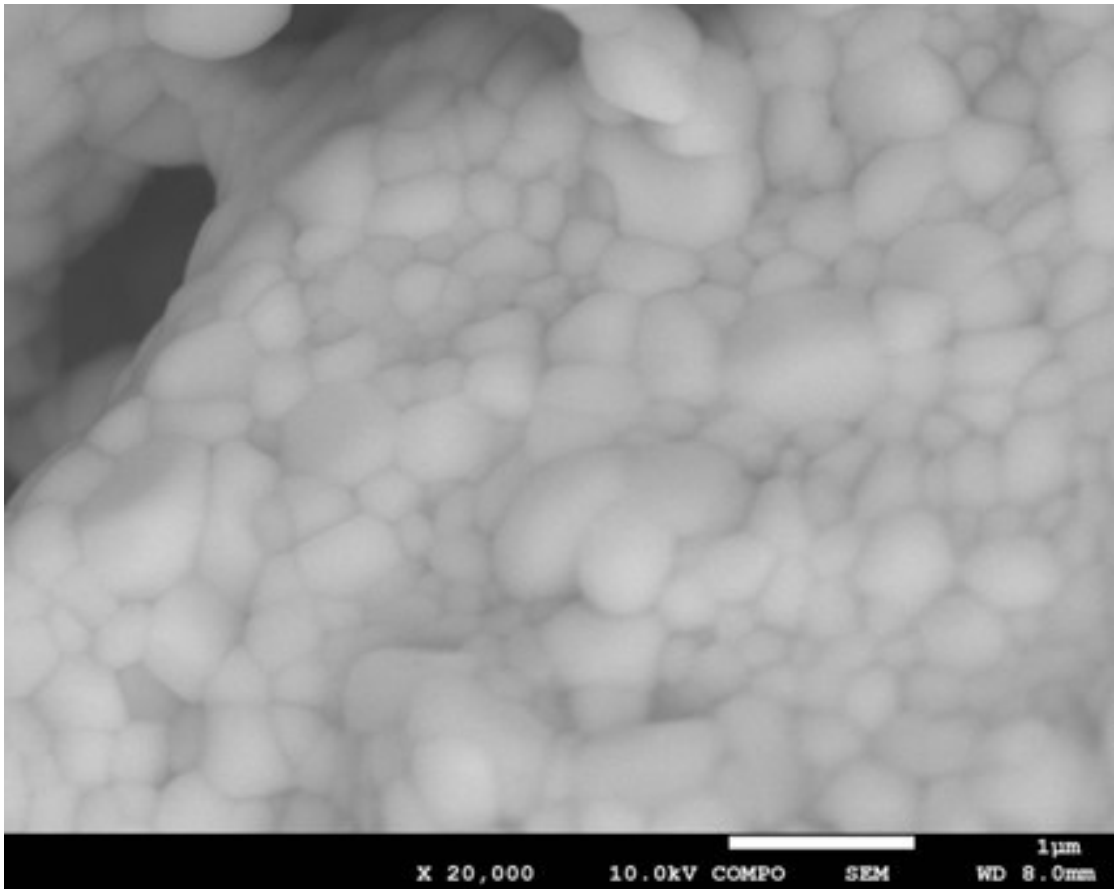

Figure S 4. SEM picture of sample ball-milled for 10h.

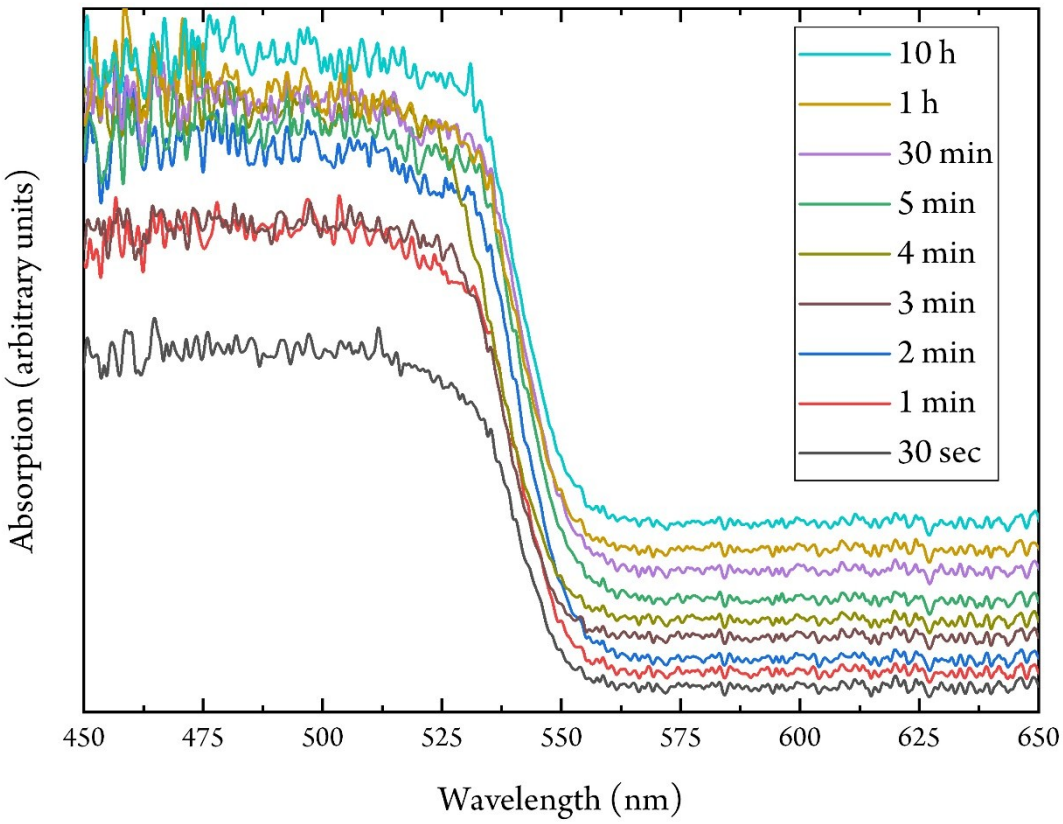

Figure S 5. Optical absorption of all samples showing similar onset around 540 nm corresponding to bulk $CsPbBr_3$.