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Supporting Information for:

Low-Dimensional Non-Toxic $A_3Bi_2X_9$ Compounds Synthesized by a Dry Mechanochemical Route with Tunable Visible Photoluminescence at Room Temperature

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EXPERIMENTAL DETAILS

Materials

Cesium chloride (CsCl, > 99 %), cesium bromide (CsBr, > 99 %) and cesium iodide (CsI, > 99 %) were purchased from TCI. Potassium chloride (KCl, ≥ 99 %), potassium bromide (KBr, > 99 %) and potassium iodide (KI, ≥ 99.5 %) were purchased from Sigma-Aldrich. Rubidium chloride (RbCl, 99.975 %), rubidium bromide (RbBr, 99.8 %) and rubidium iodide (RbI, 99.8 %) were purchased from Alfa Aeser. Methylammonium bromide (CH_3NH_3Br), methylammonium iodide (CH_3NH_3I), formamidinium chloride (CH_5N_2Cl), formamidinium bromide (CH_5N_2Br), and formamidinium iodide (CH_5N_2I) were purchased from GreatCell Solar. Methylammonium chloride (CH_3NH_3Cl, > 99.5 %) was purchased from Lumtec. All chemicals were stored in a nitrogen-filled glovebox and used as received without further purification.

Mechanochemical synthesis

AX:BiX_3 (3:2) powders (A = Cs, K, Rb, MA or FA and X = Cl, Br, or I) were mixed inside a nitrogen-filled glovebox. Then, approximately 3 grams of the mixed precursors powder was introduced inside 10 mL zirconia ball-mill jars with 2 zirconia beads of 10 mm in diameter. The jars were closed under nitrogen, preventing the powders to be exposed to air. Eventually ball milling was performed with a MM-400 straight ball-mill from Retsch, at a frequency of 30 Hz for 5 hours.

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 2 theta = 10° to 50° range in Bragg-Brentano geometry in air. Data analysis was performed with HighScore Plus and Fullprof software.

Optical characterization

Absorbance was measured with a High Power UV-VIS fiber light source, integrated sphere and Avantes Starline AVASpec-2048L spectrometer in reflection mode. Photoluminescence was measured in back-scattering geometry with excitation by Nd^{3+}YAG laser pulses at 355 nm (pulse duration 1 ns, repetition rate 1 kHz, average power 2.5 mW) and detection by USB 650 Ocean Optics spectrometer. All PL spectra were corrected for spectral sensitivity of the detection system.

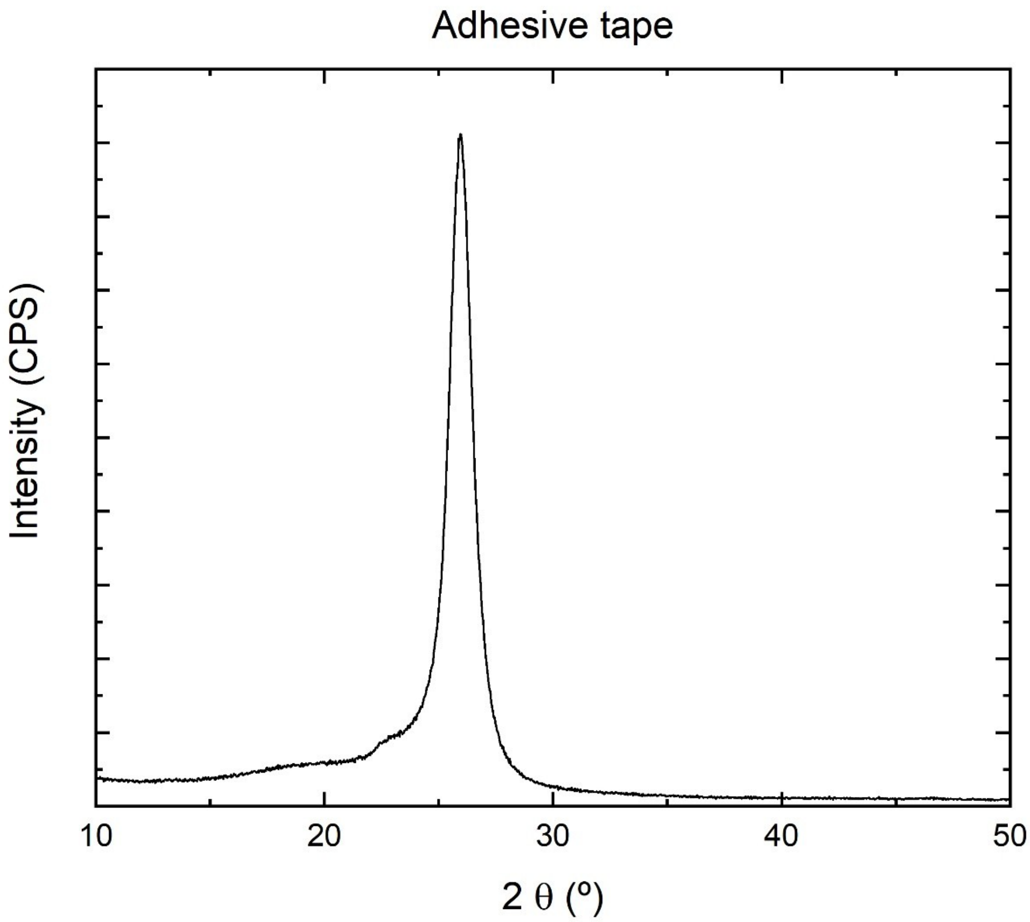

Figure S 1. XRD signal of adhesive tape used to fix the powder samples on the holder. This signal around 26º appears sometimes as a parasitic diffraction peak in the samples' diffractograms presented in Figures 1 and 3.

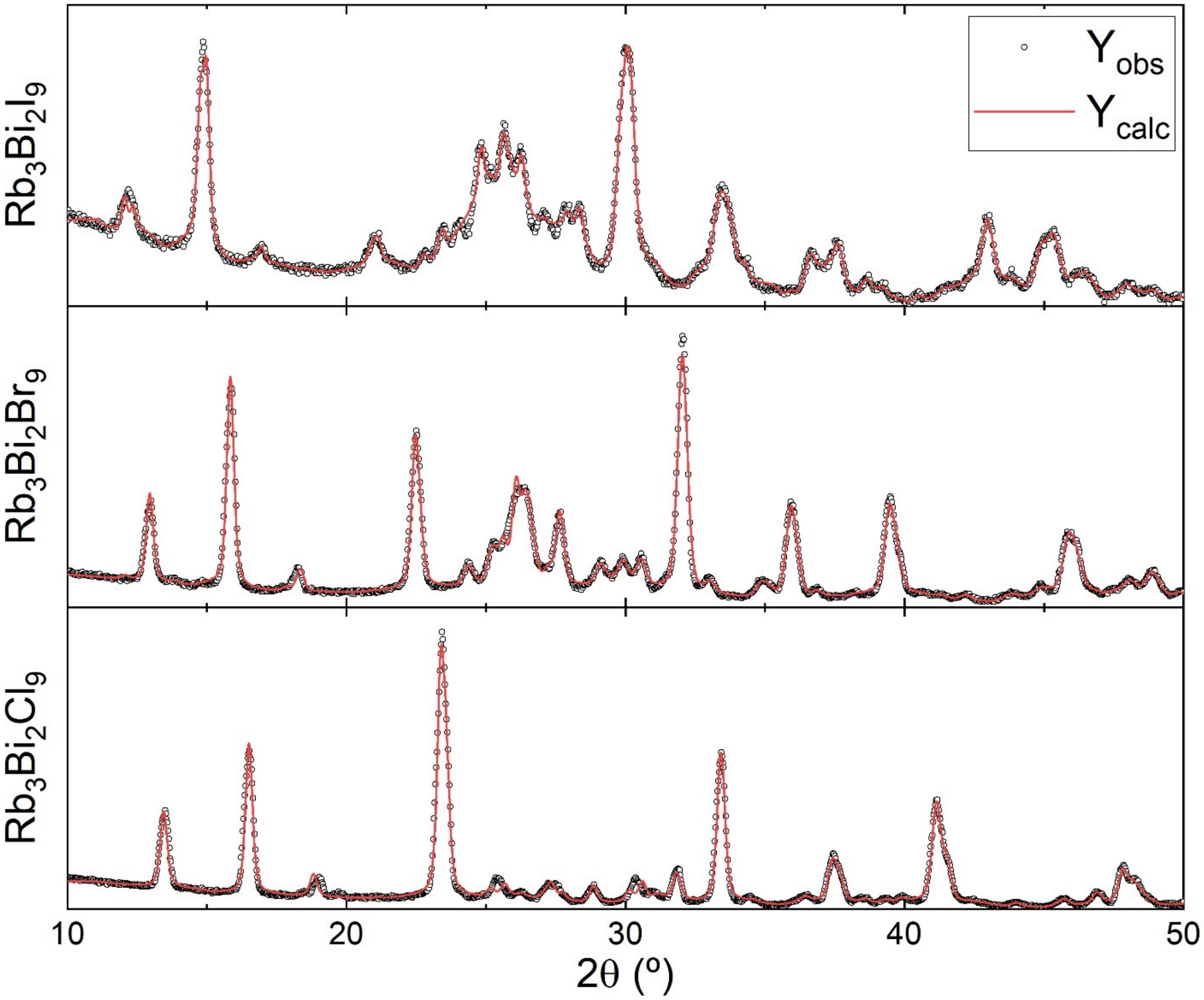

Figure S 2. Experimental and fitted XRD data for $Rb_3Bi_2X_9$ compounds. Refined lattice parameters derived from fitting are presented in Table 1.

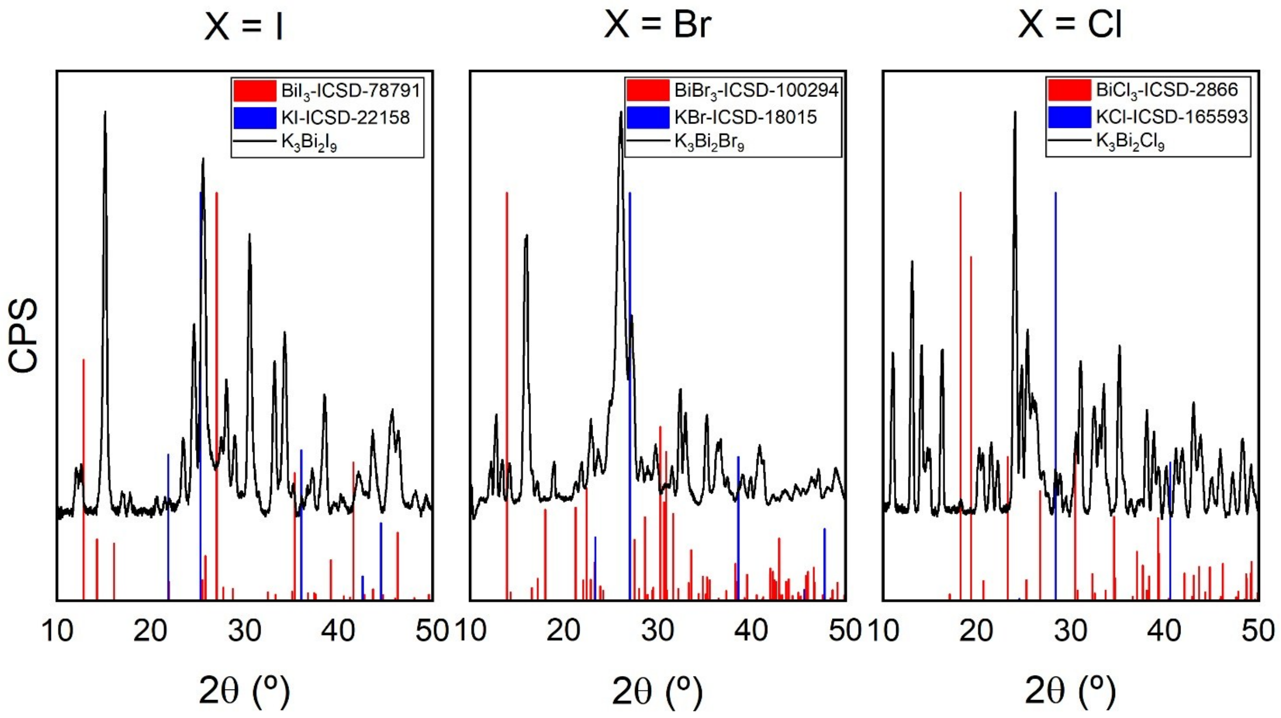

Figure S 3. Reference XRD patterns (columns) of KX and BiX_3 and diffractograms of powders obtained by ball-milling thereof. The obtained crystals are clearly different than the precursors, suggesting the reaction of the latter to form $K_3Bi_2X_9$.

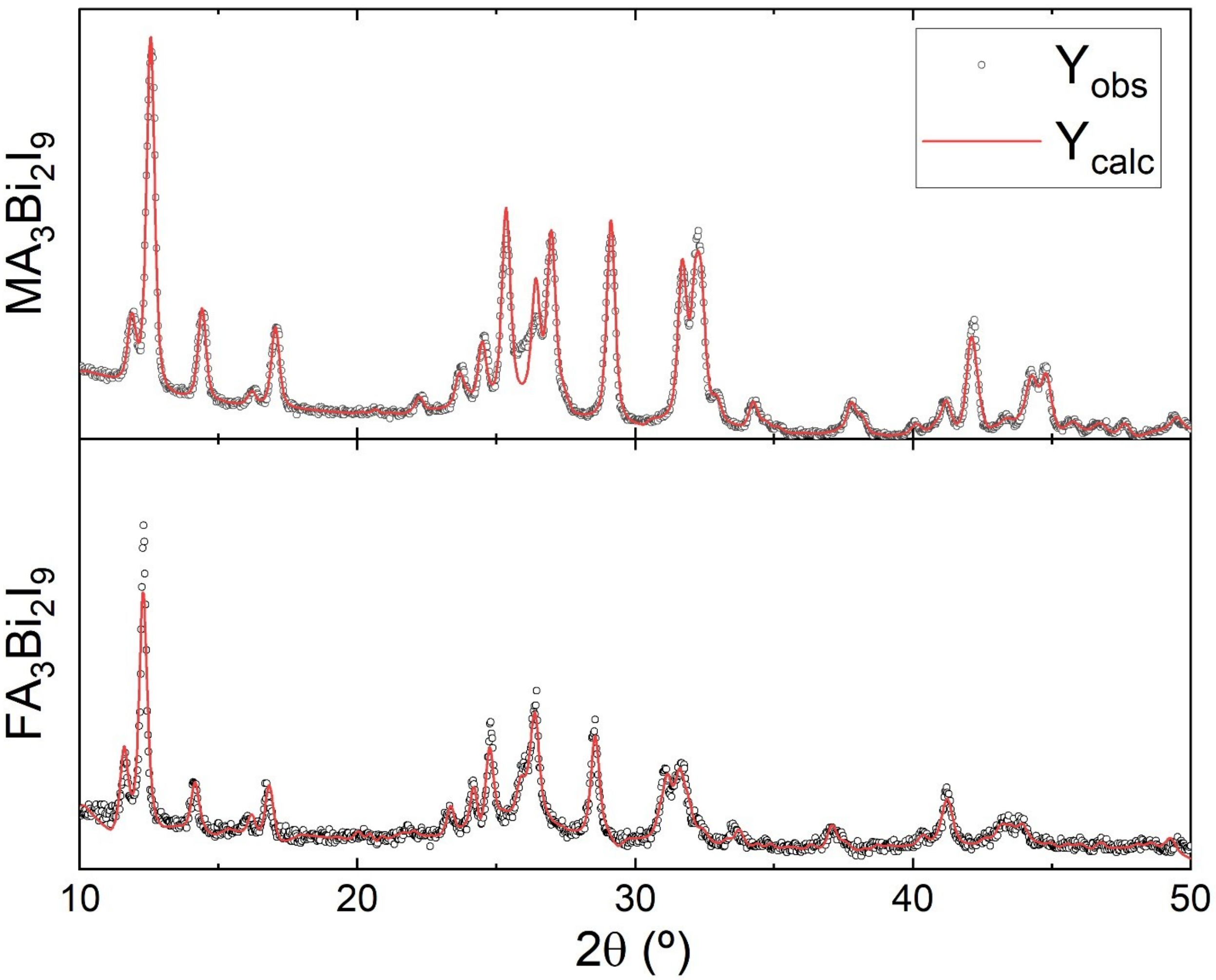

Figure S 4. Experimental and fitted data for $MA_3Bi_2I_9$ and $FA_3Bi_2I_9$. Refined cell parameters are presented in Table 2.

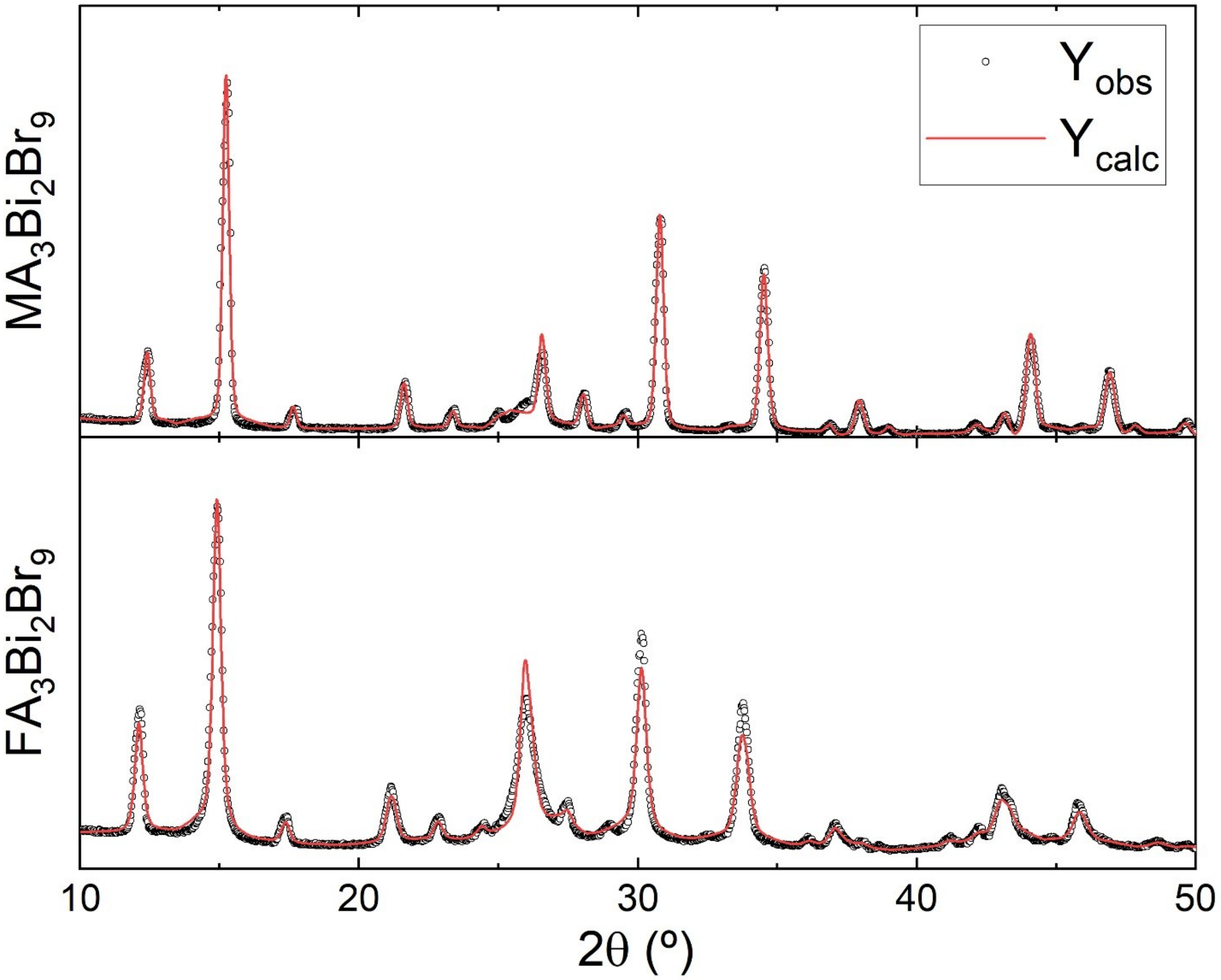

Figure S 5. Experimental and fitted data for MA$_3$Bi$_2$Br$_9$ and FA$_3$Bi$_2$Br$_9$. Refined cell parameters are presented in Table 2.

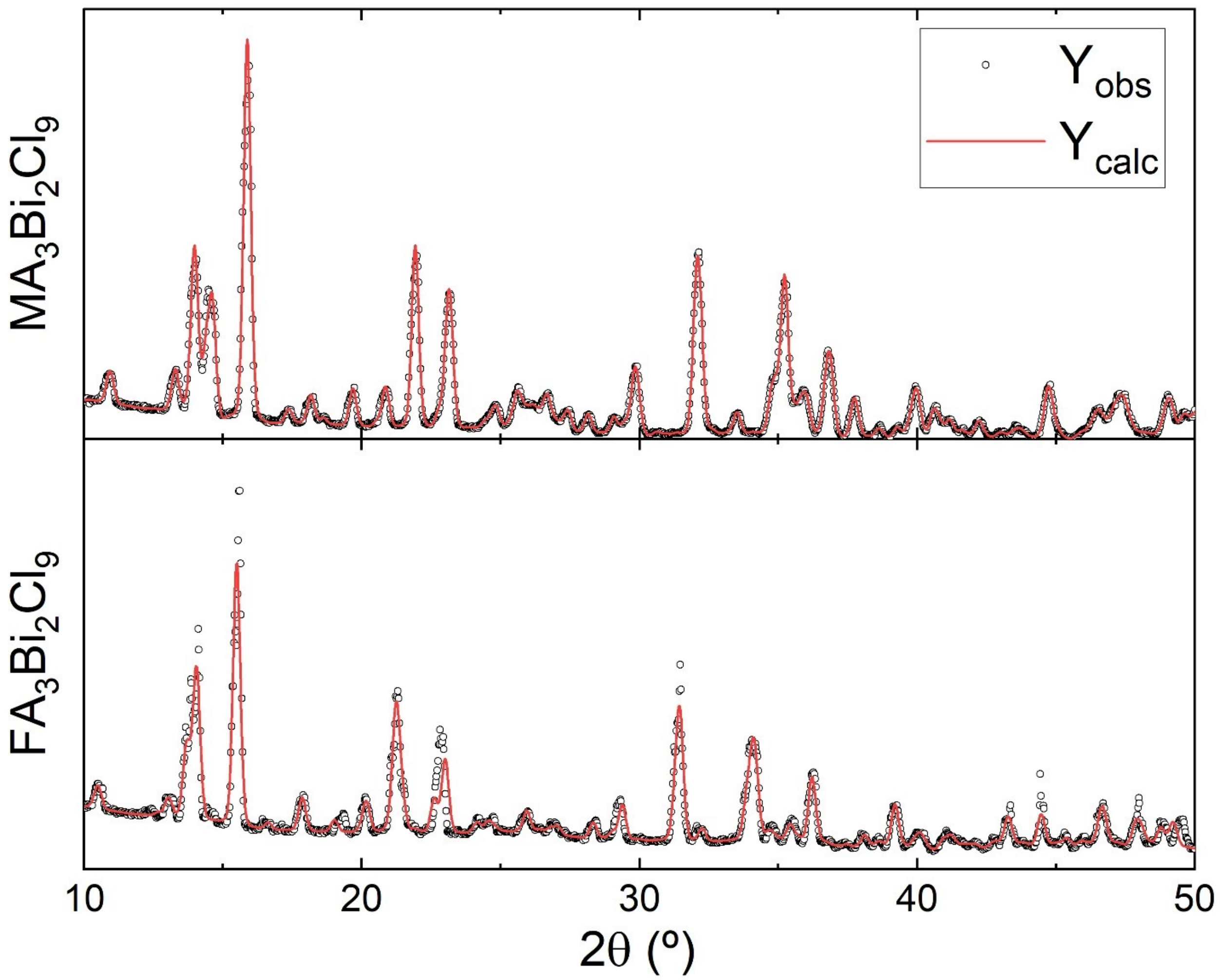

Figure S 6. Experimental and fitted data for $MA_3Bi_2Cl_9$ and $FA_3Bi_2Cl_9$. Refined cell parameters are presented in Table 2.

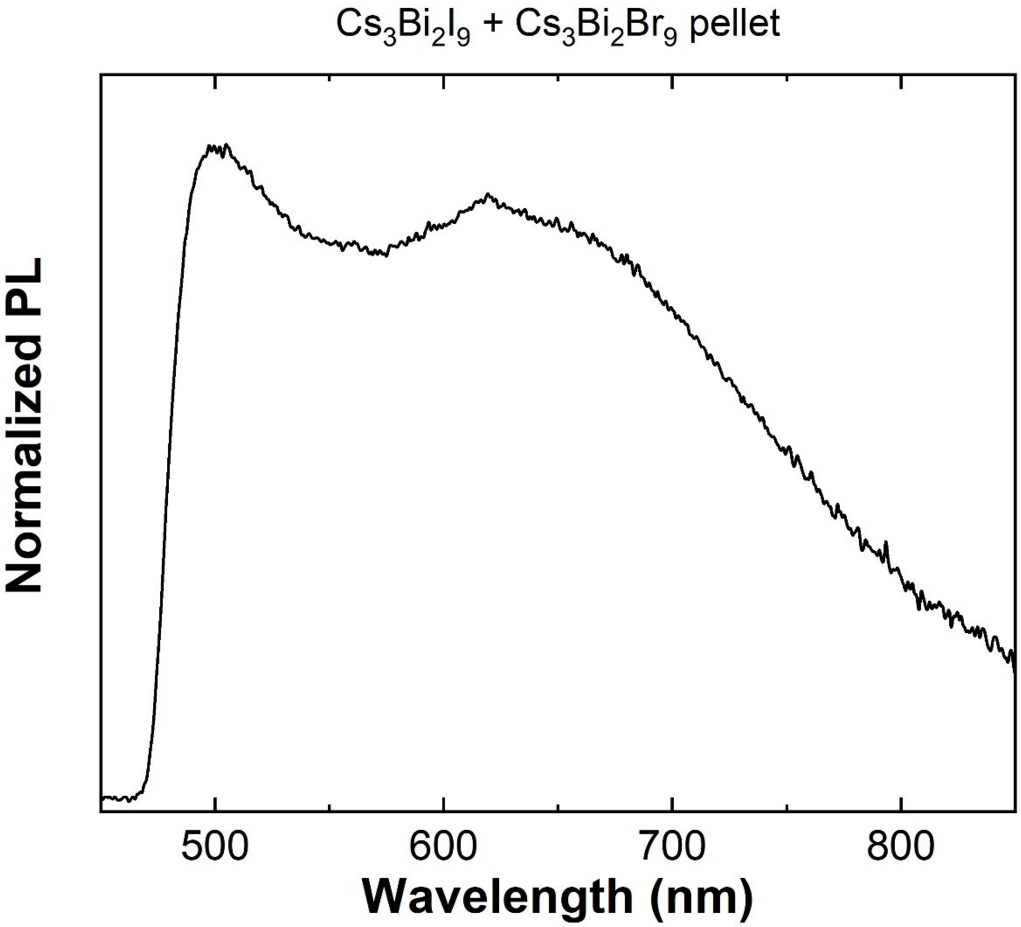

Figure S 7. PL spectrum of solid pellet made from a finely ground mixture of $Cs_3Bi_2I_9$ and $Cs_3Bi_2Br_9$ together with PMMA.