Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information for Investigation of Solution-based synthesis of Non-Toxic Perovskite Materials using Mg, Ca, Mn, Fe, Cu, and Zn as the B-site cation for Photovoltaic Applications

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EXPERIMENTAL:

Powder Synthesis:

1 molar solutions of each mixture were produced by dissolving a 1:1 ratio of AX and BX_2 salts in a 7:3 ratio of GBL and DMSO. 2 mL of solution was cast into a glass petri dish at 100 °C to anneal for one hour and form powder. Powders were stored in a sealed vial (in air) until analysis.

Table 1. Materials used in the experimental screening. Mass refers to the mass of salt used for 1 mL of solution

AX salt	Supplier	Mass (mg)	BX_2 salt	Supplier	Mass (mg)
Methylammonium iodide	Merck	159	Magnesium Iodide	Merck	278
Methylammonium bromide	Merck	112	Magnesium Bromide	Merck	184
Potassium iodide	Alfa Aesar	166	Calcium Iodide	Merck	294
Potassium bromide	Alfa Aesar	119	Manganese bromide	Merck	215
Rubidium iodide	Alfa Aesar	165	Iron bromide	Merck	216
Rubidium bromide	Alfa Aesar	212	Iron iodide	Merck	310
			Copper bromide	Alfa Aesar	223
			Zinc iodide	Merck	320

Solutions were then diluted to 1 mmol for attempted single crystal synthesis through solvent evaporation. No successful crystals were produced during this work.

Thin-Film Synthesis:

For thin-film synthesis, solutions were made in the same way as for powder preparation. 100 µL of solution were cast onto cleaned glass slides, and spin-coated at 2000 rpm for 20 seconds. Films were annealed at 100 °C for 1 hour. Films were stored in air until analysis.

Solar Cell Synthesis:

FTO was etched to the desired pattern using Zn powder (Merck) and 2M HCl (Merck). Substrates were cleaned under sonication at 60 °C using deionised water, acetone, and isopropanol. 35 µL of filtered PEDOT:PSS (Ossila) was spin-coated at 6000 rpm for 40 seconds and heated to 100 °C. 100 µL of perovskite solution was deposited at 2000 rpm for 20 seconds, then annealed at 100 °C for 1 hour. A 20 mgml^{-1} solution of $PC_{71}BM$ (Ossila) was deposited at 3000 rpm for 30 seconds.

A silver (Alfa Aesar) contact was added by metal evaporation.

XRD:

X-ray diffraction patterns were obtained using a Bruker D2 Phaser X-ray diffractometer, fitted with a 1-dimensional Lynxeye detector and a copper X-ray source (K_α = 1.54184Å) operated at 30 kV and 10mA. K_β radiation was suppressed by means of a 0.5mm thick nickel filter. Patterns were recorded over a range of 5 – 50° (2θ) with a step size of 0.02° and an equivalent time of 96 seconds per step. Sample rotation was set at 15 rpm.

Microscopy:

Scanning electron microscopy was carried out on a JEOL JSM-7100F Field Emission Scanning Electron Microscope (FE-SEM). Samples were sputter coated with gold/palladium to provide a 5 to 10nm conductive layer to facilitate analysis. Images were collected using an accelerating voltage of 5kV and an approximate beam current of 120pA. Energy-dispersive X-ray spectroscopy (EDS) used an Oxford Instruments X-max 80mm^2 detector, combined with AzTec software, allowing elemental analysis to be carried out. Microscope parameters for EDS were changed to an accelerating voltage of 20kV and beam current of approximately 1nA.

UV/Vis:

Thin-film UV/Vis analysis was performed on a Cary5000 UV/Vis/NIR spectrometer. The measurements were taken in %Reflectance mode between 800 nm and 350 nm using an integrating sphere attachment. The Kubelka-Munk function was used to obtain band gap information from reflectance data.

PV Characterisation:

The J-V characteristics were measured using an ABET solar simulator in the dark and under illumination with Class A AM1.5G spectral match, calibrated using a reference Si photodiode. Measurements were taken at 0.7 Sun. Simulator uses a xenon arc lamp, and all the measurements were performed at room temperature.

Supplementary Data:

STAGE 1:

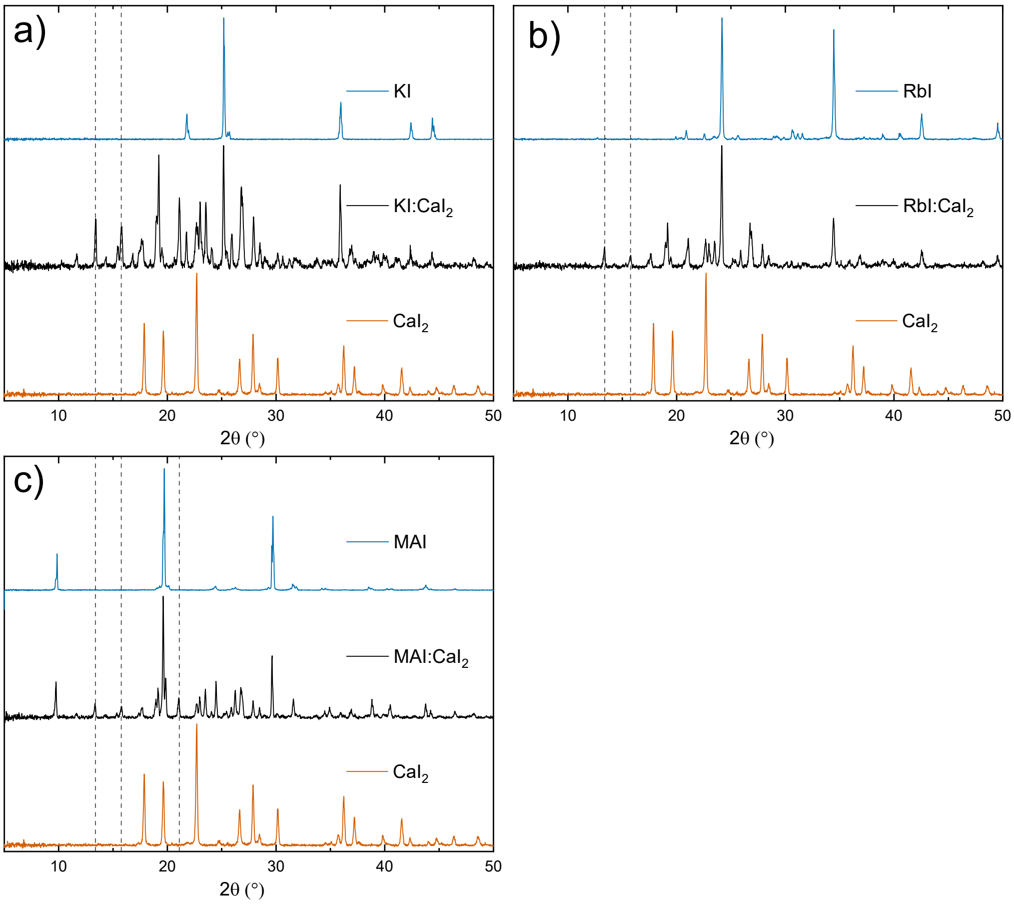

Figure S1. Normalised PXRD patterns for materials using calcium as the B-site cation and *a)* potassium, *b)* rubidium and *c)* methylammonium as the A-site cation. Dashed lines show major peaks un-matched to starting materials.

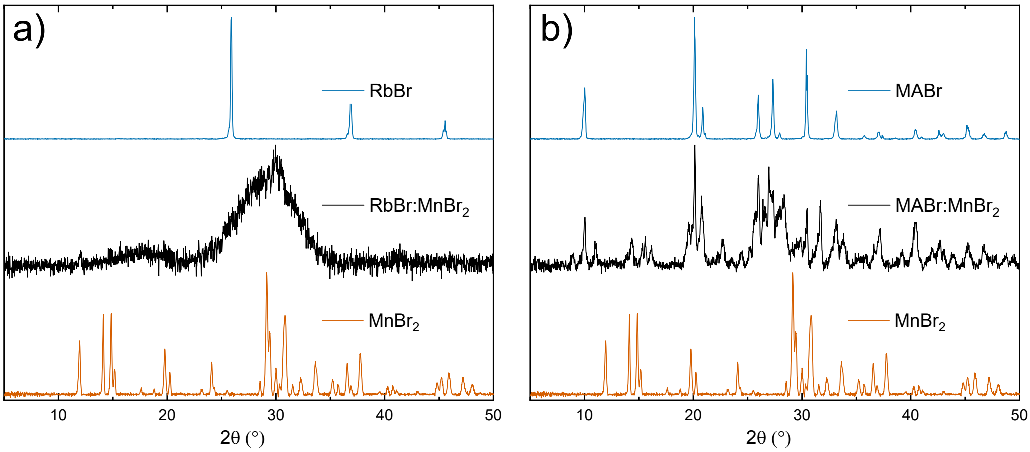

Figure S2. Normalised PXRD patterns for materials using manganese as the B-site cation and *a)* potassium and b*)* methylammonium as the A-site cation. Dashed lines show major peaks un-matched to starting materials. (Using K^+ as a cation did not produce a viable powder)

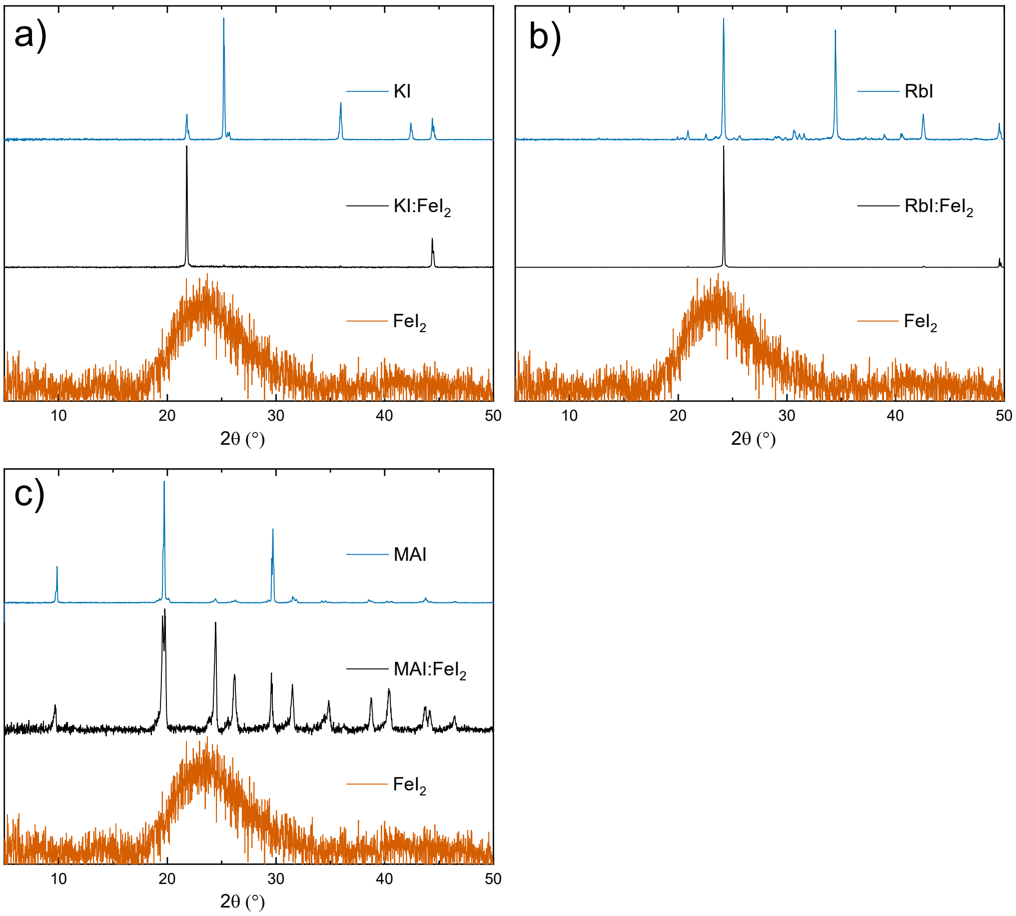

Figure S3. PXRD patterns for materials using iron as the B-site cation, iodide as the X-site anion and *a)* potassium, *b)* rubidium and *c)* methylammonium as the A-site cation. Dashed lines show major peaks un-matched to starting materials.

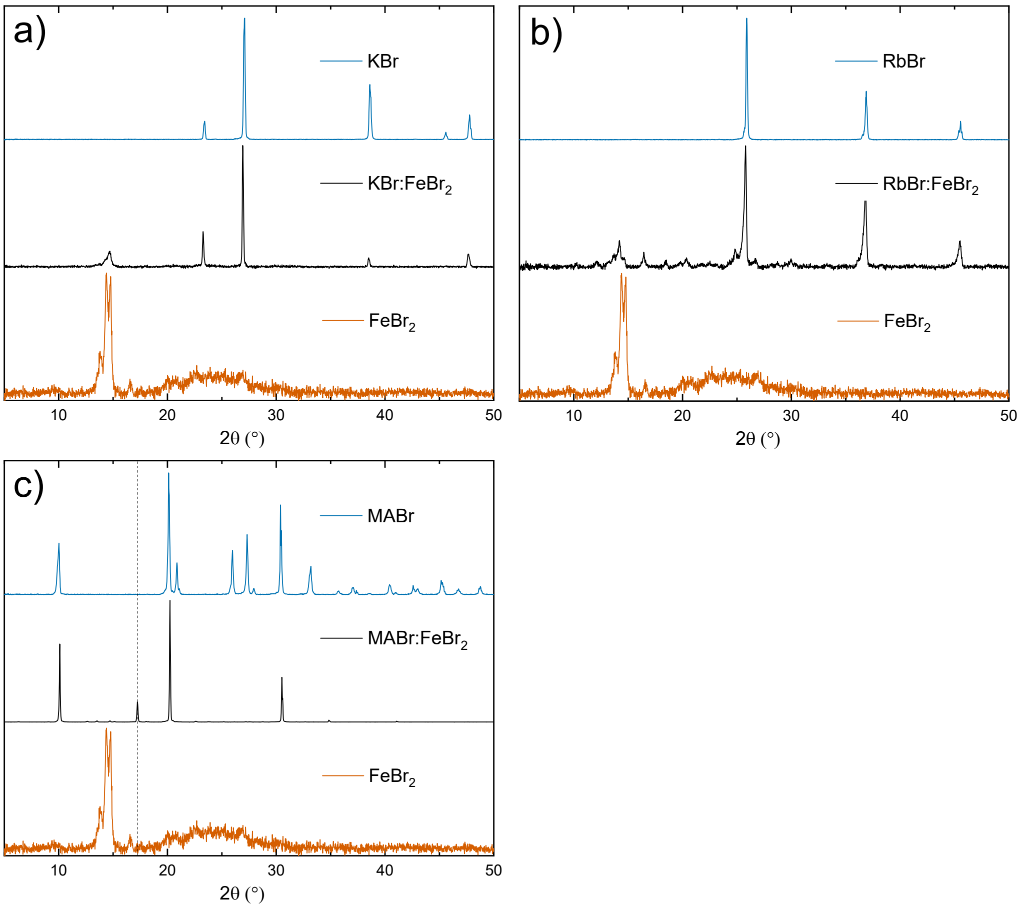

Figure S4. Normalised PXRD patterns for materials using iron as the B-site cation, bromide as the X-site anion and *a)* potassium, *b)* rubidium and *c)* methylammonium as the A-site cation. Dashed lines show major peaks un-matched to starting materials.

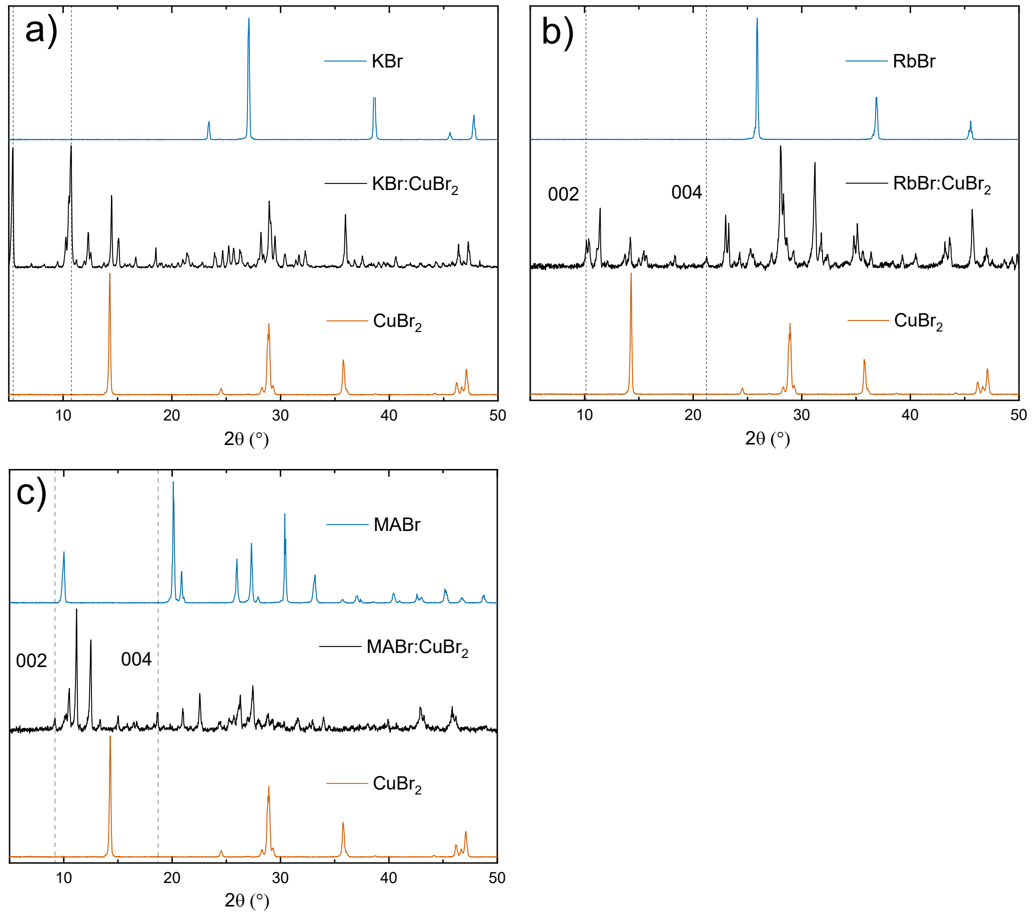

Figure S5. Normalised PXRD patterns for materials using copper as the B-site cation and *a)* potassium, *b)* rubidium and *c)* methylammonium as the A-site cation. Dashed lines show major peaks un-matched to starting materials. Reflections have been taken from reference[1]. $CsCuX_n$ peaks used for the rubidium containing compound.

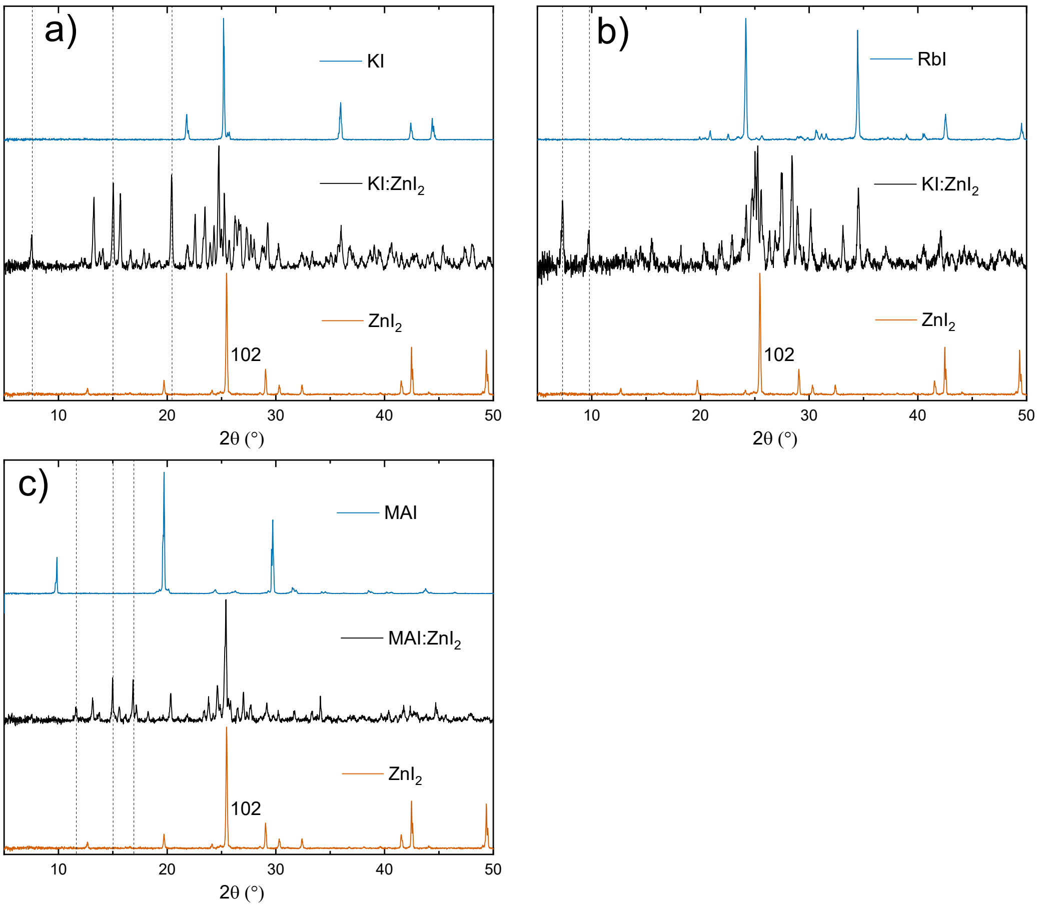

Figure S6. Normalised PXRD patterns for materials using zinc as the B-site cation and *a)* potassium, *b)* rubidium and *c)* methylammonium as the A-site cation. Dashed lines show major peaks un-matched to starting materials. Data for ZnI_2 102 reflection taken from reference[2].

STAGE 2:

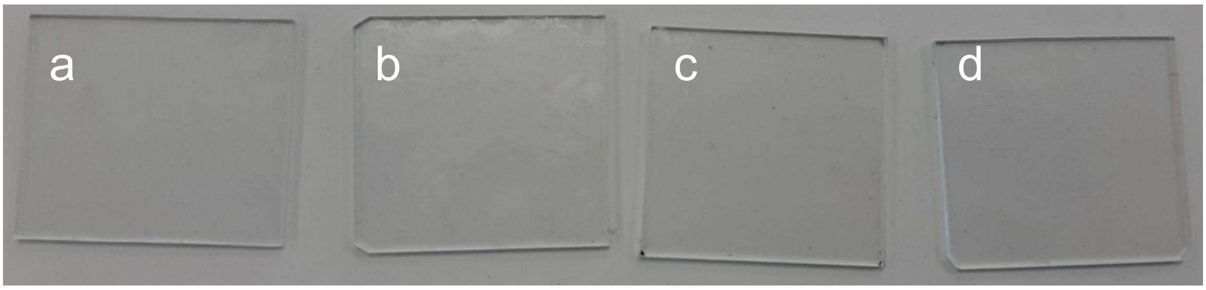

Figure S7. Images of CaI_2 based thin films containing, a) blank microscope slide, b) K, c) Rb and d) MA as the A-site cation.

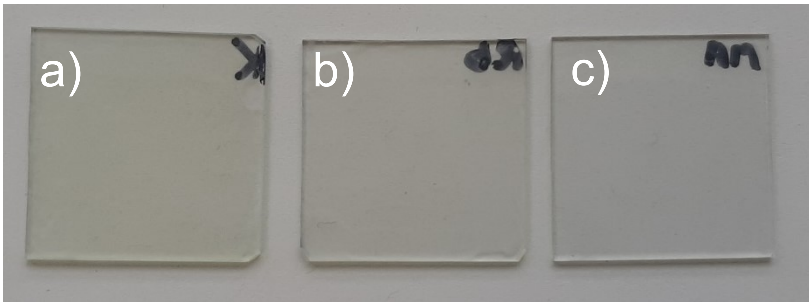

Figure S8. Images of $CuBr_2$ based thin films containing, a) K, b) Rb and c) MA as the A-site cation.

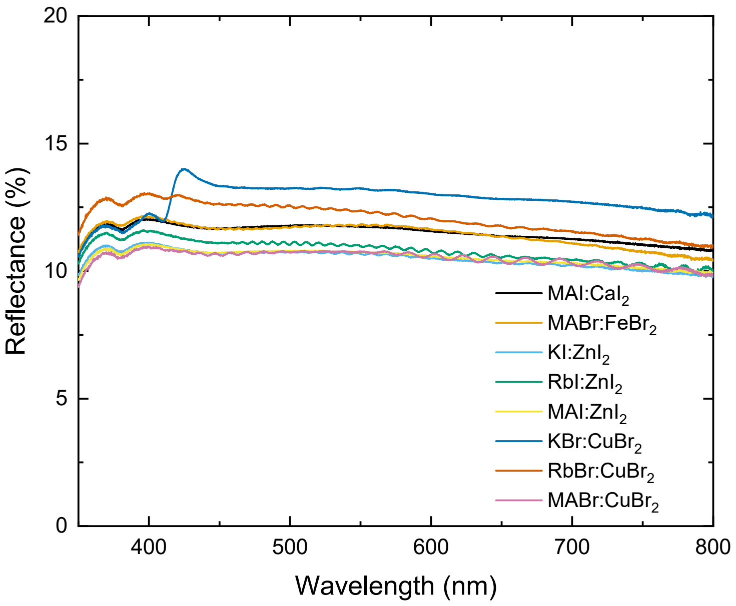

Figure S9. UV/Vis Reflectance for thin-film materials in stage 2 analysis

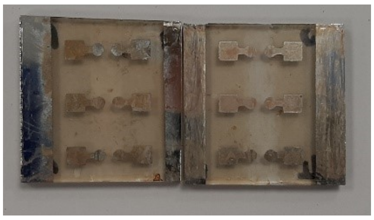

Figure S10. Photograph of devices using KBr:$CuBr_2$ as the potential absorber material.

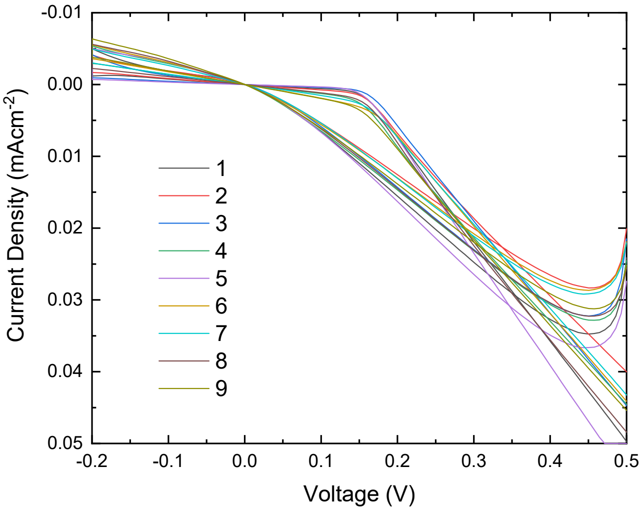

Figure S11. JV curves for samples that showed a suitable response (3/12 only showed resistor behaviour). The number in the legend refers to a different pixel on the device.

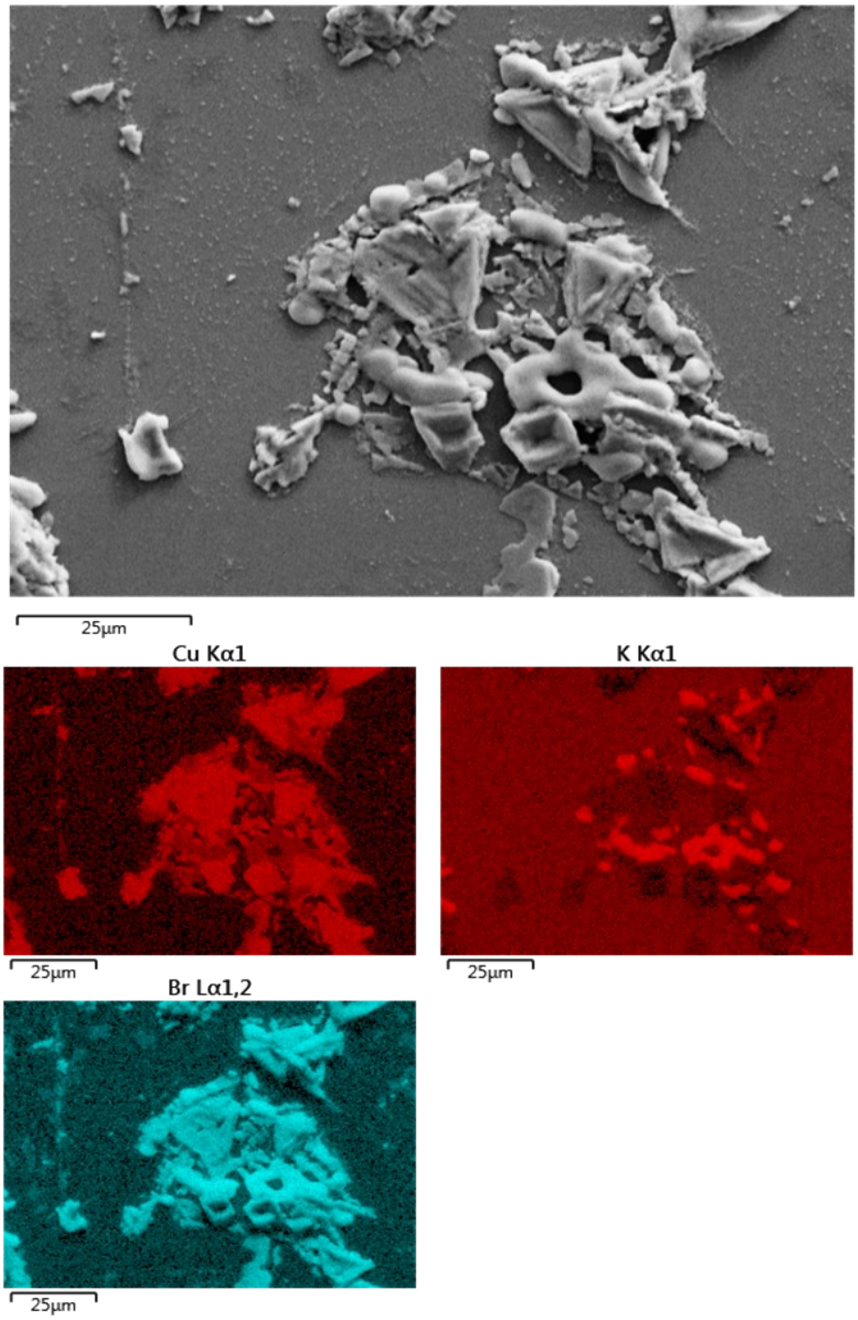

Figure S12. SEM/EDS analysis of KBr:$CuBr_2$

1. D. Cortecchia, H. A. Dewi, J. Yin, A. Bruno, S. Chen, T. Baikie, P. P. Boix, M. Grätzel, S. Mhaisalkar, C. Soci, and N. Mathews, *Inorg. Chem.*, 2016, **55**, 1044–1052.

2. P. Tyagi and A. G. Vedeshwar, *Phys. Rev. B*, 2001, **64**, 245406.