Supplementary Information

Table S1. A comparison of crystallographic parameters of Rb_2AgX_3 (X = Br,Cl)

Crystallographic Parameters	**Rb_2AgBr_3[1]**	**Rb_2AgCl_3[2]**
Crystal System	Orthorhombic	Orthorhombic
Space Group	Pnma	Pnma
a (Å)	4.68	4.49
b (Å)	9.65	9.22
c (Å)	18.76	17.88
α/β/γ (°)	90	90

Table S2. The XPS fitting results and calculated surface atomic percentage of Rb_2AgBr_3.

Elements	**Rb**		**Ag**		**Br**	
Peak binding energy (eV)	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$
	109.7	111.3	368.2	374.2	68.4	69.5
Surface Atomic Percentage (%)	28.7		11.6		30.5	

Table S3. The XPS fitting results and calculated surface atomic percentages of Rb_2AgCl_3.

Elements	**Rb**		**Ag**		**Cl**	
Peak binding energy (eV)	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$2p_{3/2}$	$2p_{1/2}$
	109.7	111.1	368.2	374.2	198.0	199.7
Surface Atomic Percentage (%)	33.8		15.2		39.2	

Table S4. λ_{max} values from fitted PL data of Rb_2AgX_3 pellets series pressed at pressures ranging from 124.8 to 499.4 MPa against recorded powder values.

Rb_2AgX_3	**PL λ_{max} / nm**				
	0 MPa	*124.8 MPa*	*249.7 MPa*	*374.5 MPa*	*499.4 MPa*
Rb_2AgCl_3	585	587	589	591	594

Rb_2AgBr_3	514	502	514	514	520

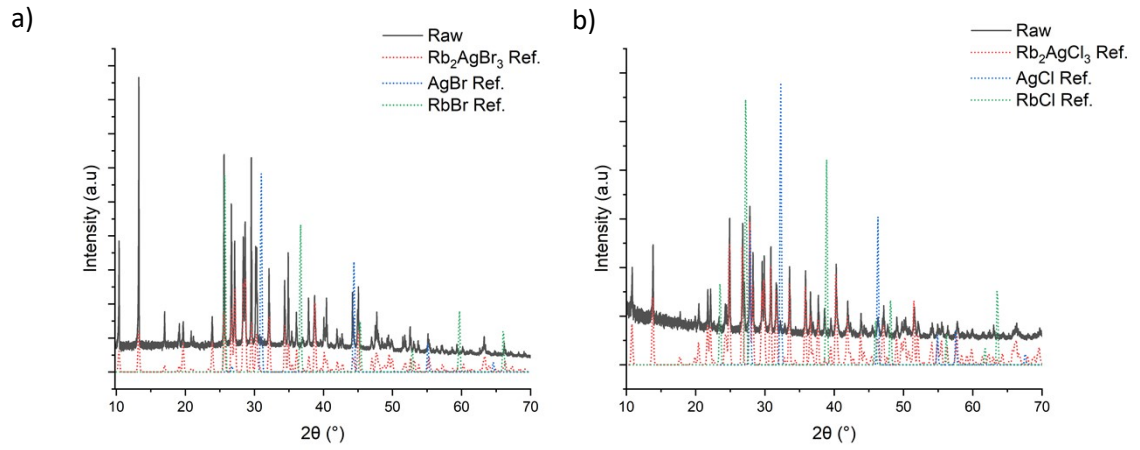

Figure S1. PXRD patterns of a) Rb_2AgBr_3 and b) Rb_2AgCl_3 as-synthesised powders compared to known references of precursor salts sourced from the ICSD database.[33]

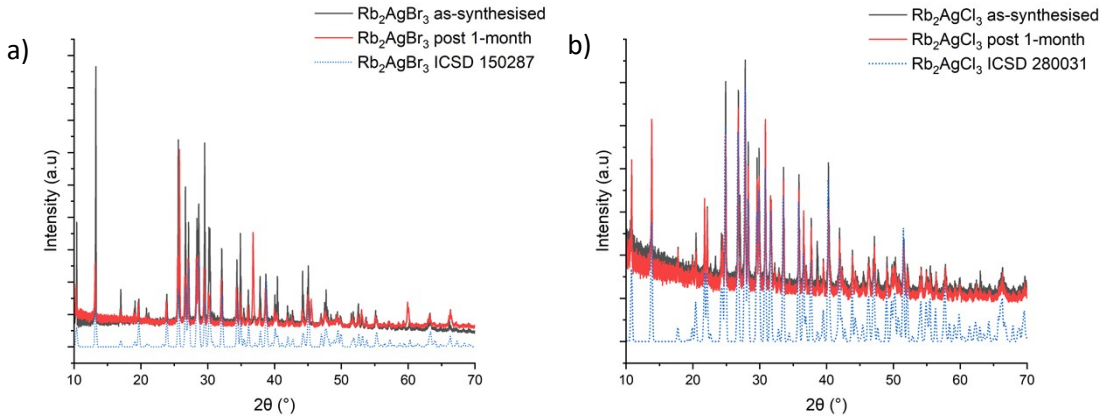

Figure S2. PXRD patterns of a) Rb_2AgBr_3 and b) Rb_2AgCl_3 depicting as-synthesised powders versus 1-month later accompanied by their respective reference patterns from the ICSD database.[33]

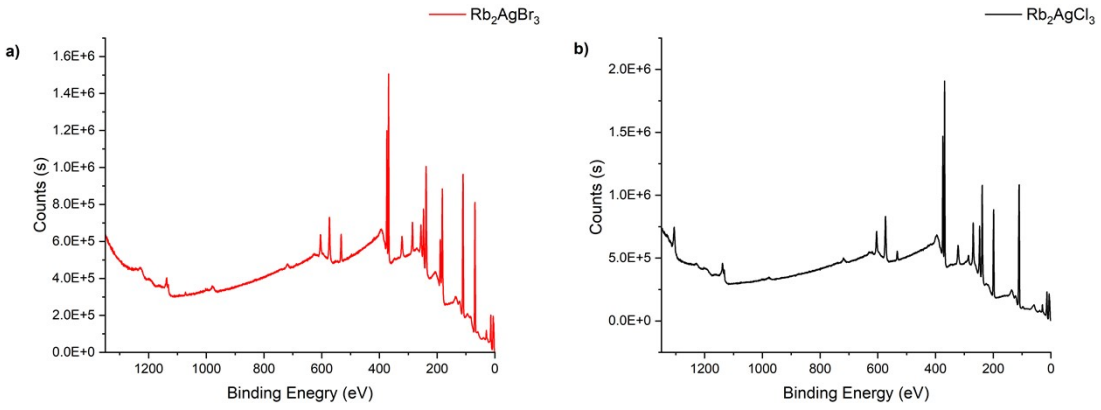

Figure S3. XPS survey spectra of a) Rb_2AgBr_3 and b) Rb_2AgCl_3

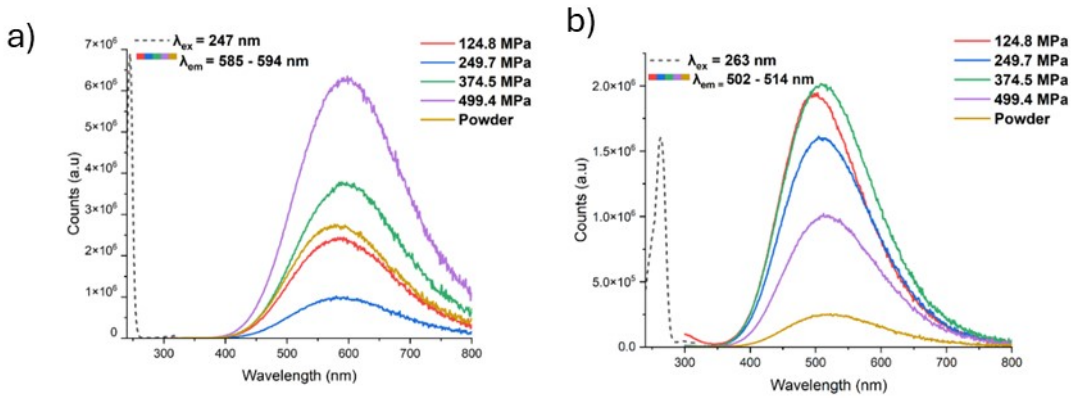

Figure S4. PL spectra of pellets of a) Rb_2AgCl_3 and of b) Rb_2AgBr_3 across pressures ranging 124.8 to 499.4 MPa compared against PL data from powder measurements.

Thermal stability measurements of Rb_2AgX_3

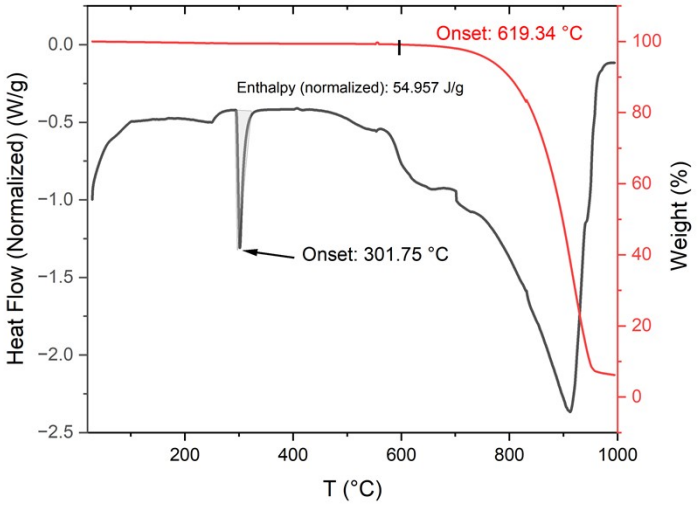

Figure S5. Thermal stability measurement of Rb_2AgCl_3 depicting thermal gravimetric analysis (TGA) data (red) overlaid with differential scanning calorimetry (DSC) data (black). Both sets of measurements were run in tandem under a N_2 flowing atmosphere from RT to 1000 °C at 10 °C/min.

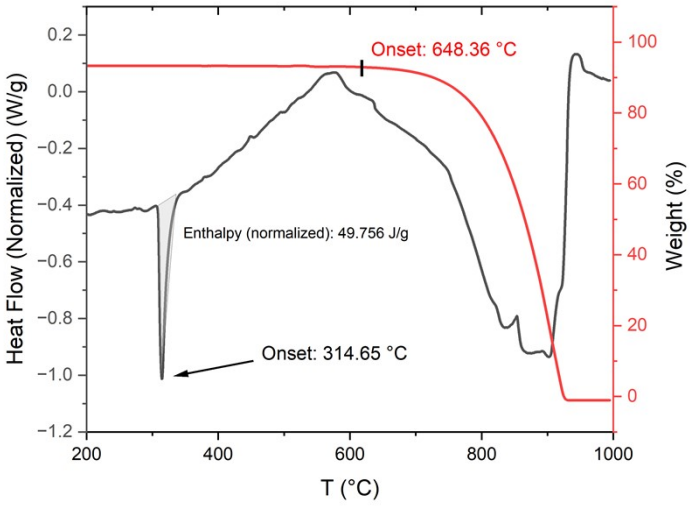

Figure S6. Thermal stability measurement of Rb_2AgBr_3 depicting thermal gravimetric analysis (TGA) data (red) overlaid with differential scanning calorimetry (DSC) data (black). Both sets of measurements were run in tandem under a N_2 flowing atmosphere from RT to 1000 °C at 10 °C/min.

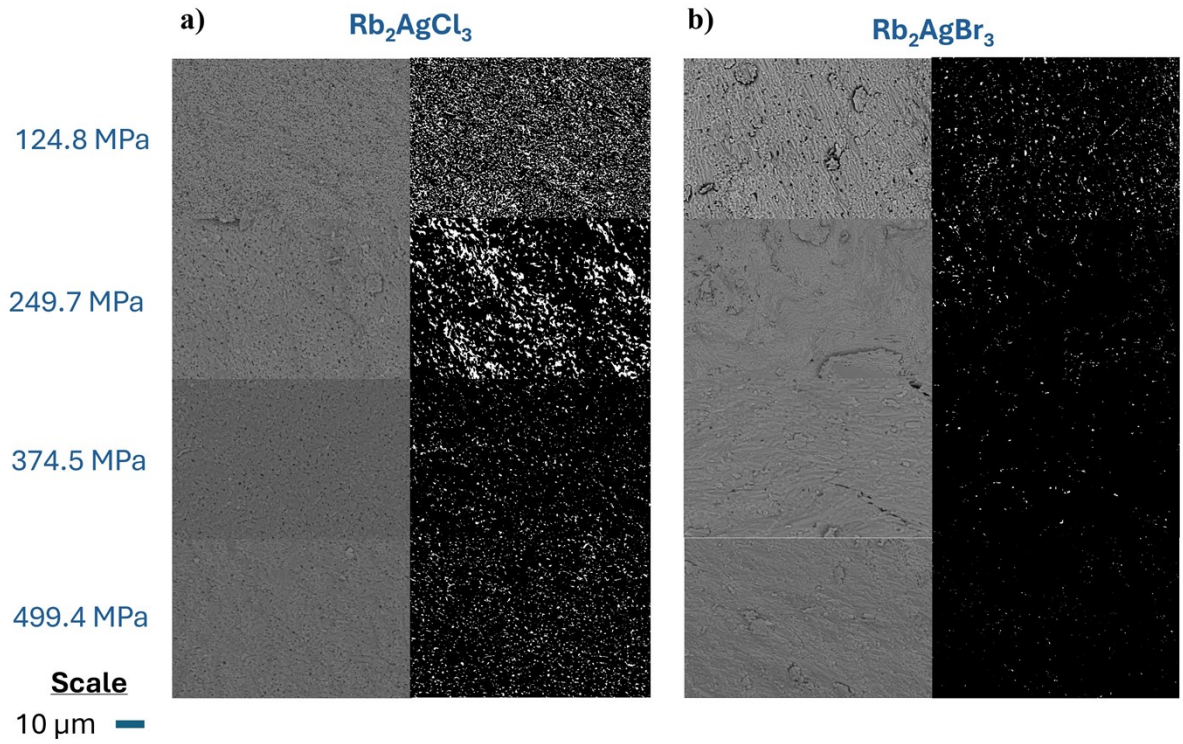

Figure S7. Cross-sectional SEM backscatter electron (BSE) images (LHS) of a) Rb2AgCl3 and b) Rb2AgBr3 10 mm Ø pellets illustrating the change in microstructure with increasing pressure from 124.8 MPa to 499.4 MPa. Images (RHS) rendered via ImageJTM showing pores (white) amongst the bulk of the material (black) that highlight the changes in void density with variation in pressure.

[1] S. Hull and P. Berastegui, J Solid State Chem, 2004, 177, 3156–3173.
[2] C. Hasselgren and S. Jagner, Acta Crystallogr C, 1999, 55, 1208–1210.