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

Synthesis, crystal chemistry, and optical properties of two methylammonium silver halides: $CH_3NH_3AgBr_2$ and $CH_3NH_3Ag_2I_3$

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Supporting Information:

Table S1. Single crystal XRD data for $CH_3NH_3AgBr_2$ and $CH_3NH_3Ag_2I_3$.

Empirical formula	$CH_3NH_3AgBr_2$	$CH_3NH_3Ag_2I_3$
Temperature	296.15 K	296.15 K
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma*	$P2_1/m$
Unit cell dimensions	a = 9.0387(11) Å	a = 9.019(3) Å
	b = 4.6831(5) Å	b = 6.329(2) Å
	c = 14.7759(13) Å	c = 9.134(3) Å
	$\alpha = 90^\circ$	$\alpha = 90^\circ$
	$\beta = 90^\circ$	$\beta = 110.431(10)^\circ$
	$\gamma = 90^\circ$	$\gamma = 90^\circ$
Volume	625.45(12) Å^3	488.6(3) Å^3
Z	4	2

Density (calculated)	3.183 g/cm^3	4.272 g/cm^3
Absorption coefficient	15.857 mm^{-1}	13.404 mm^{-1}
F(000)	544.0	544.0
Crystal size	0.451 × 0.123 × 0.067 mm^3	0.183 × 0.109 × 0.087 mm^3
Crystal color, habit	Colorless plate	Colorless plate
2 Theta range for data collection	5.284 to 50.988°	4.76 to 50.856°
Index ranges	$-10 \le h \le 7$, $-5 \le k \le 4$, $-17 \le l \le 17$	$-10 \le h \le 10$, $-7 \le k \le 7$, $-11 \le l \le 11$
Reflections collected	2651	5985
Independent reflections	656 [R(int) = 0.0270, R(sigma) = 0.0240]	992 [R(int) = 0.0383, R(sigma) = 0.0303]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	656 / 0 / 33	992 / 0 / 42
Goodness-of-fit on F^2	0.922	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.1105	R1 = 0.0357, wR2 = 0.0890
R indices (all data)	R1 = 0.0443, wR2 = 0.1161	R1 = 0.0509, wR2 = 0.0947
Largest diff. peak and hole	0.69 and −1.80 e Å^{-3}	0.87 and −1.43 e Å^{-3}

Table S2. Fractional atomic coordinates, equivalent isotropic displacement parameters, and chemical occupancy for $CH_3NH_3AgBr_2$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atom	Wyckoff Site	x	y	z	U_{eq} (Å^2)	Occupancy
Ag	4c	0.52170(10)	0.7500	0.41899(4)	0.0701(4)	1
Br(1)	4c	0.37286(9)	0.7500	0.26412(5)	0.0524(3)	1
Br(2)	4c	0.67197(10)	0.2500	0.43483(5)	0.0527(3)	1
N	4c	0.6145(8)	0.2500	0.1976(4)	0.0612(19)	1
C	4c	0.6057(14)	0.2500	0.1002(5)	0.081(3)	1
H(1)	8d	0.5371	0.3428	0.2204	0.073	0.5
H(2)	8d	0.6976	0.3363	0.2149	0.073	0.5
H(3)	8d	0.6144	0.0709	0.2177	0.073	0.5
H(4)	8d	0.5191	0.3532	0.0814	0.122	0.5
H(5)	8d	0.5997	0.0569	0.0787	0.122	0.5
H(6)	8d	0.6922	0.3400	0.0755	0.122	0.5

Table S3. Bond lengths for $CH_3NH_3AgBr_2$.

Atom	Atom	Length(Å)
Ag01	Br02	2.654(1)
Ag01	Br03[3]	2.7171(6)
Ag01	Br03[1]	2.780(1)
Ag01	Br03	2.7171(6)
N004	C005	1.442(9)
[1]1-X,1-Y,1-Z; [2]1-X,2-Y,1-Z; [3]+X,1+Y,+Z		

Table S4. Bond angles for $CH_3NH_3AgBr_2$.

Atom	Atom	Atom	Angle(°)
Br02	Ag01	Br03[1]	110.53(4)
Br02	Ag01	Br03	109.12(2)
Br02	Ag01	Br03[2]	109.12(2)
Br03	Ag01	Br03[1]	104.35(3)
Br03[2]	Ag01	Br03	119.04(4)
Br03[2]	Ag01	Br03[1]	104.35(3)
[1]1-X,1-Y,1-Z; [2]+X,1+Y,+Z			

Table S5. Fractional atomic coordinates, equivalent isotropic displacement parameters, and chemical occupancy for $CH_3NH_3Ag_2I_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor**.**

Atom	Wyckoff Site	x	y	z	U_{eq} (Å^2)	Occupancy
I(1)	2e	0.43266(9)	0.7500	0.11181(9)	0.0549(3)	1
I(2)	2e	–0.08120(8)	0.7500	0.14806(8)	0.0523(2)	1
I(3)	2e	0.28412(10)	0.2500	0.41270(9)	0.0593(3)	1
Ag	4f	0.18624(8)	0.49961(12)	0.14033(8)	0.0698(3)	1
N	2e	0.6416(13)	0.2500	0.3137(12)	0.090(4)	1
C	2e	0.8132(14)	0.2500	0.3701(13)	0.070(4)	1
H(1)	4f	0.6063	0.3814	0.2896	0.108	0.5
H(2)	4f	0.6081	0.1998	0.3877	0.108	0.5
H(3)	4f	0.6052	0.1688	0.2290	0.108	0.5
H(4)	4f	0.8525	0.3390	0.4606	0.105	0.5
H(5)	4f	0.8494	0.3025	0.2898	0.105	0.5
H(6)	4f	0.8513	0.1086	0.3973	0.105	0.5

Table S6. Bond lengths for $CH_3NH_3Ag_2I_3$.

Atom	Atom	Length(Å)
I001	Ag00[1]	2.8149(12)
I001	Ag00	2.8149(12)
I002	Ag00[1]	2.9076(12)
I002	Ag00	2.9076(12)
I002	Ag00[2]	2.9307(12)
I002	Ag00[3]	2.9307(12)
I003	Ag00[4]	2.8161(12)
I003	Ag00	2.8161(12)
N005	C1	1.450(14)
[1]+X,3/2-Y,+Z; [2]-X,1/2+Y,-Z; [3]-X,1-Y,-Z; [4]+X,1/2-Y,+Z		

Table S7. Bond angles for $CH_3NH_3Ag_2I_3$.

Atom	Atom	Atom	Angle(°)
I001	Ag00	I002[1]	103.79(3)
I001	Ag00	I002	112.58(4)
I001	Ag00	I003	112.54(3)
I002	Ag00	I002[1]	107.76(3)
I003	Ag00	I002[1]	113.25(4)
I003	Ag00	I002	106.93(3)
[1]-X,1-Y,-Z			

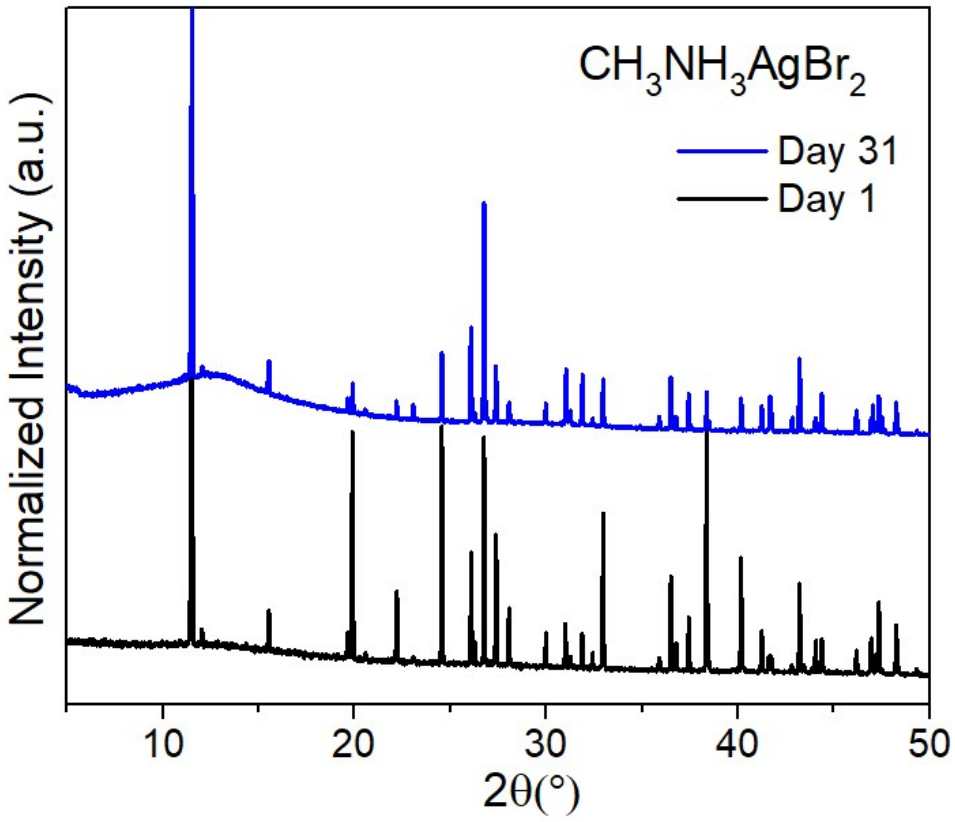

Figure S1. PXRD of $CH_3NH_3AgBr_2$ measured after synthesis (black) and after ~1 month (blue). Changes that are observed appear to be due to different preferred orientation effects. The lack of any new peaks indicates stability under ambient conditions.

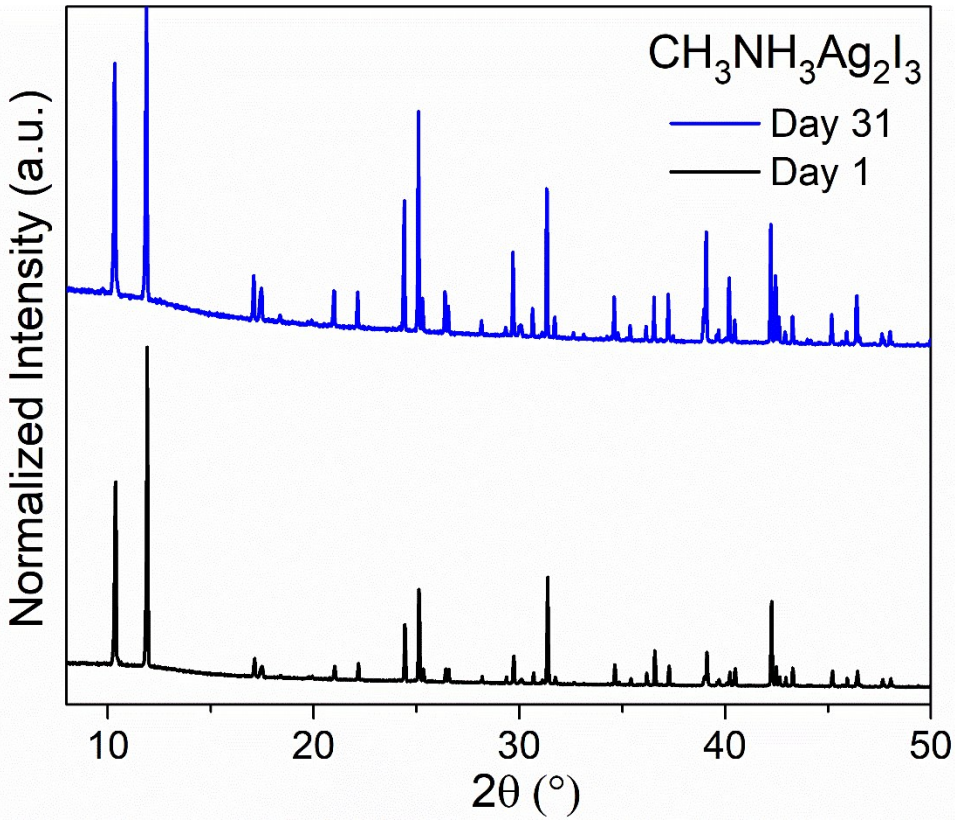

Figure S2. PXRD of $CH_3NH_3Ag_2I_3$ measured after synthesis (black) and after ~1 month (blue). Minimal changes are observed, indicating stability towards ambient conditions.

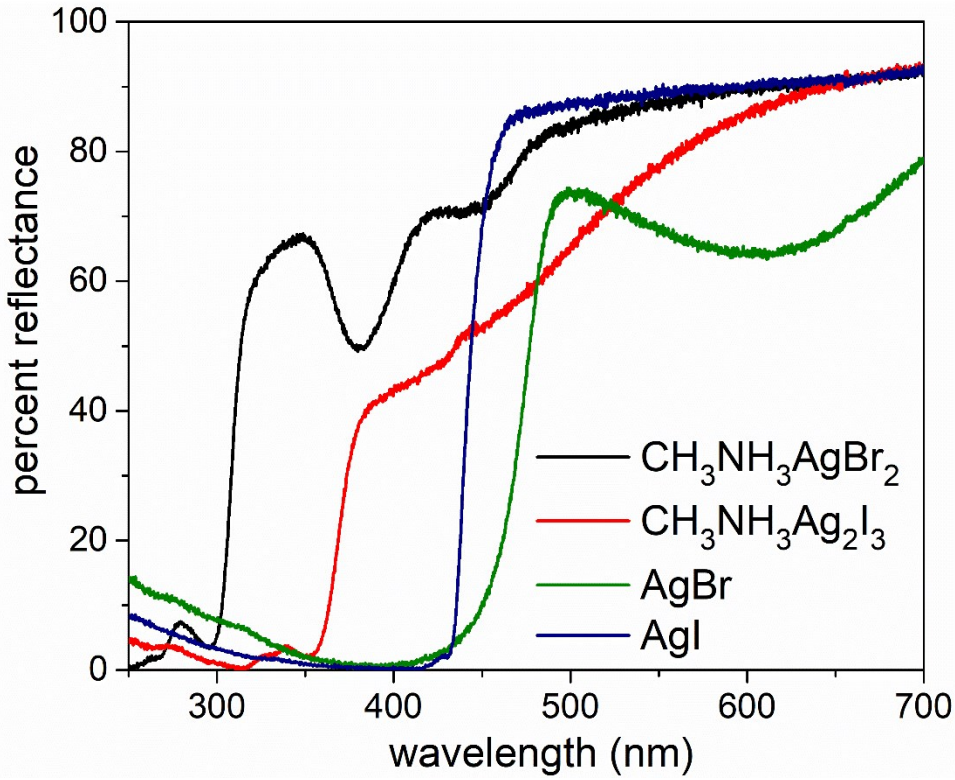

Figure S3. Diffuse reflectance data for the ternary phases and the silver halide starting materials. A blue shift in absorption is observed, in part due to decreased electronic dimensionality.

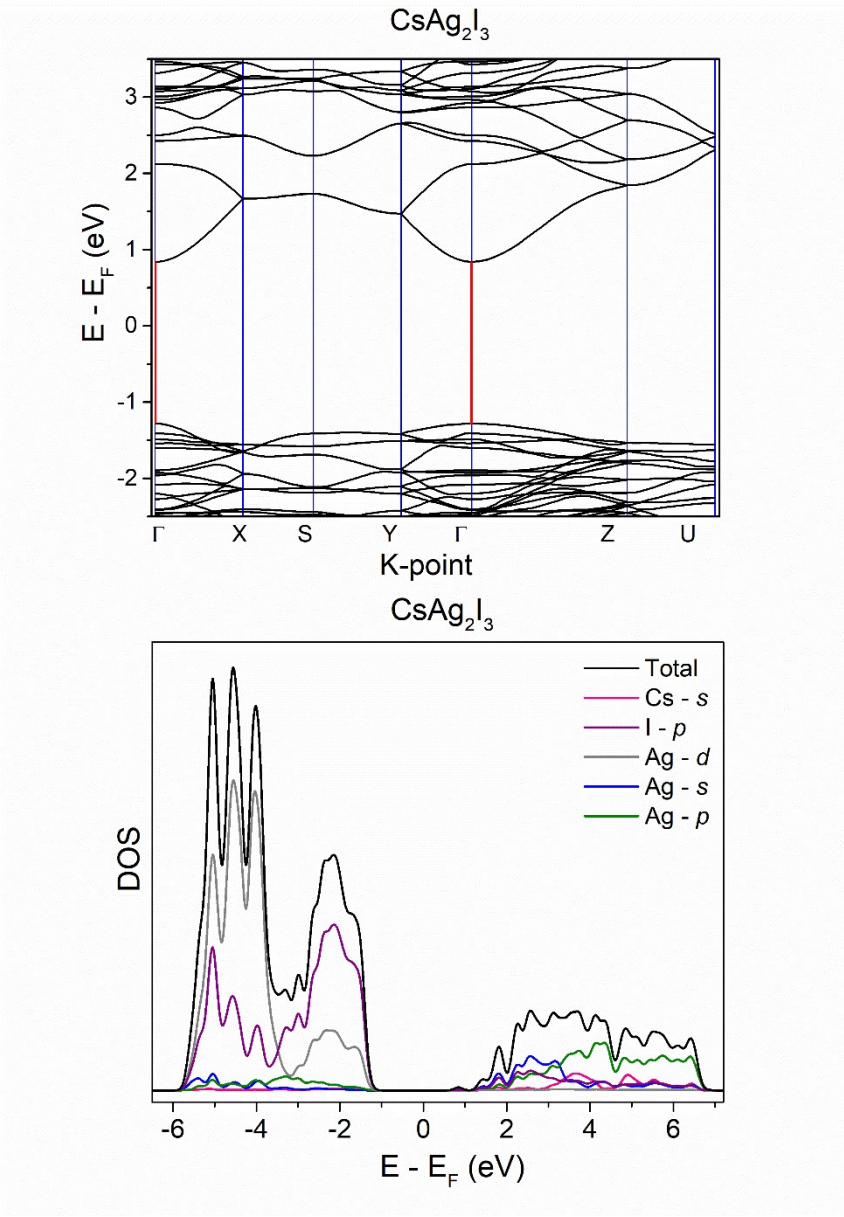

Figure S4. (Top) Band structure of $CsAg_2I_3$. The k–points are highlighted in blue and the direct transition at the Γ-point is highlighted in red. (Bottom) Total and partial DOS for $CsAg_2I_3$.

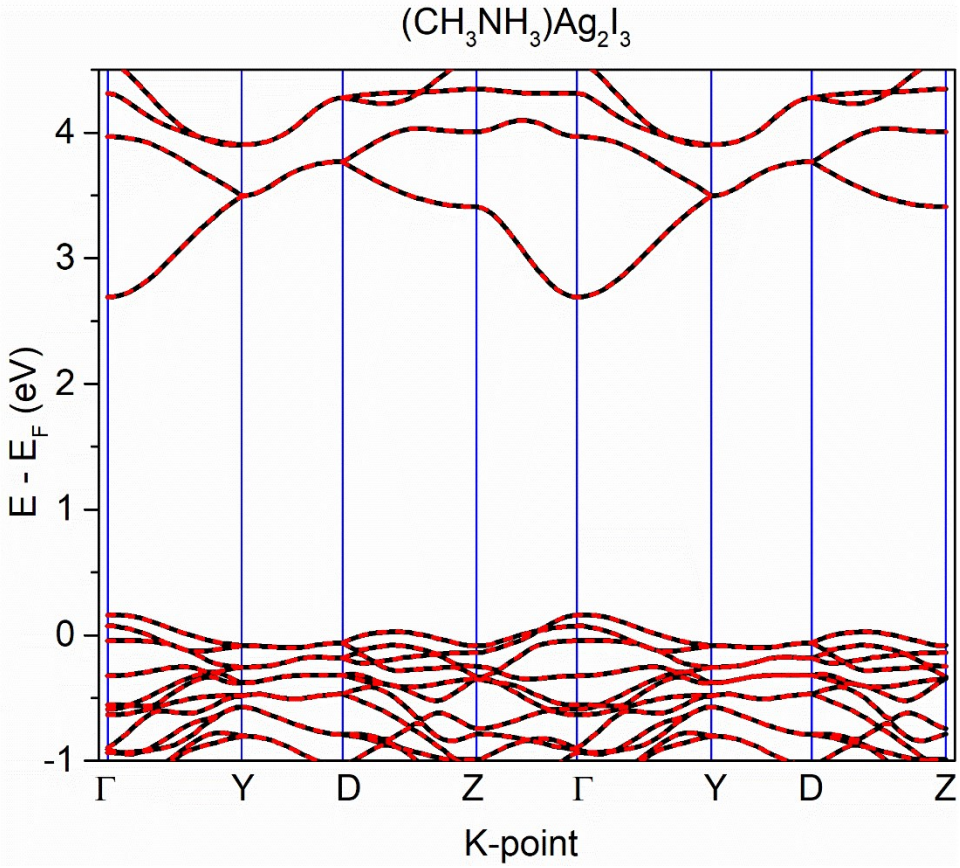

Figure S5. Comparison of $CH_3NH_3Ag_2I_3$ with and without spin orbit coupling (SOC). Red dashed line represents calculation performed with SOC. Minimal changes were observed, indicating SOC has a minor effect on the band dispersion in the frontier bands.

Table S8. List of related ternary (Rb/Cs/(CH_3NH_3))-(Ag/Cu)-(Cl/Br/I) phases. Coordination environment of the polyhedra are provided. A (*) denotes an observed polyhedral distortion.

Compound	Space Group	*a* (Å)	*b* (Å)	*c* (Å)	Ag^+ Coordination	Reference	ICSD #
Rb_2AgCl_3	*Pnma*	9.205	4.482	17.874	tetrahedra	1	280031
Rb_2AgBr_3	*Pnma*	9.577	4.646	18.663	tetrahedra	2	150287
Rb_2AgI_3	*Pnma*	10.238	4.898	19.984	tetrahedra	2	150290
$CsAgCl_2$	*Cmcm*	4.376	19.186	5.685	square pyramid*	2	150299
Cs_2AgCl_3	*Pnma*	13.210	4.551	13.758	tetrahedra*	2	150286
Cs_2AgBr_3	*Pnma*	13.755	4.719	14.362	tetrahedra	2	150288
$CsAgBr_2$	*Cmcm*	4.574	19.894	5.947	square pyramid*	2	150301
Cs_2AgI_3	*Pnma*	14.588	4.951	15.298	tetrahedra	2	150291
$CsAg_2I_3$	*Pbnm*	11.076	13.743	6.231	tetrahedra	2	150308
K_2CuCl_3	*Pnma*	12.030	4.148	12.587	tetrahedra	2	150292
K_2CuBr_3	*Pnma*	12.607	4.336	13.247	tetrahedra	2	150293
Rb_2CuCl_3	*Pnma*	12.501	4.272	13.000	tetrahedra	2	150294
Rb_2CuBr_3	*Pnma*	13.073	4.452	13.641	tetrahedra	2	150295
$CH_3NH_3AgBr_2$	*Pnma*	9.0387	4.6831	14.776	tetrahedra	this work	-
$CH_3NH_3Cu_2I_3$	$P2_1/m$	8.9053	5.8982	9.077	tetrahedra	3	263606
$CH_3NH_3Ag_2I_3$	$P2_1/m$	9.019	6.329	9.134	tetrahedra	this work	-

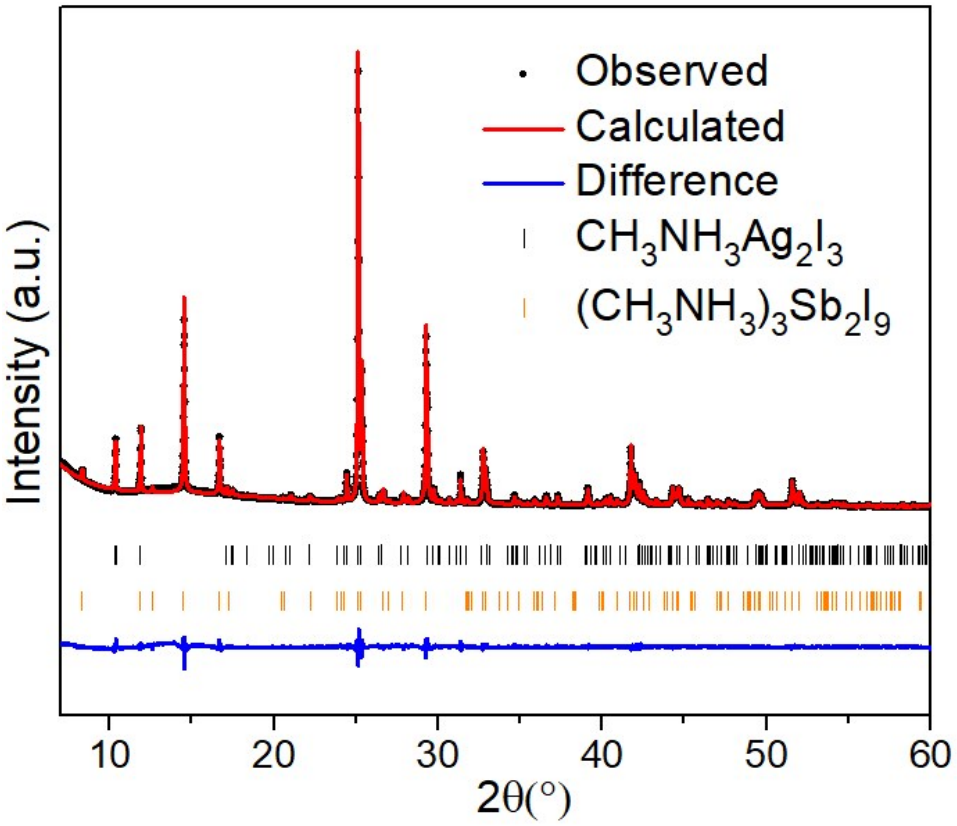

Figure S6. Pawley refinement of "$(CH_3NH_3)_2AgSbI_6$", fit to $CH_3NH_3Ag_2I_3$ and $(CH_3NH_3)_3Sb_2I_9$. Observed, calculated and difference curves are plotted with black dots, a red line, and a blue line, respectively. $CH_3NH_3Ag_2I_3$ is denoted by black tick marks, while $(CH_3NH_3)_3Sb_2I_9$ is denoted by orange tick marks.

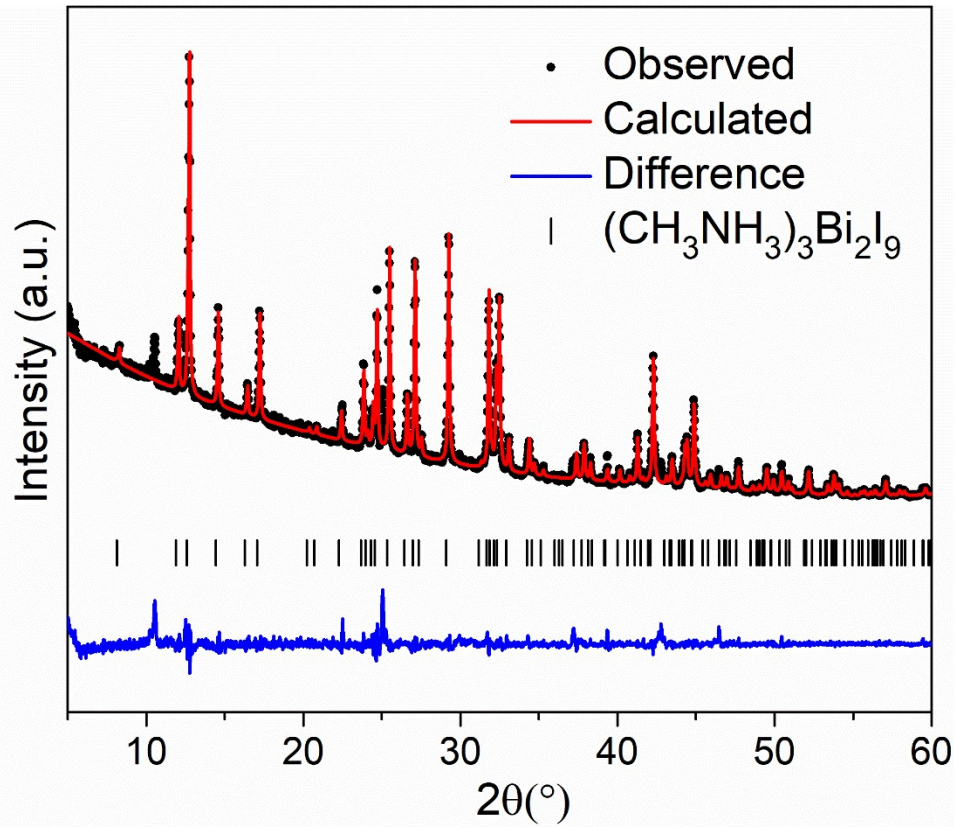

Figure S7. Pawley refinement of "$(CH_3NH_3)_2AgBiI_6$", fit to $(CH_3NH_3)_3Bi_2I_9$. Observed, calculated and difference curves are plotted with black dots, a red line, and a blue line, respectively. $(CH_3NH_3)_3Sb_2I_9$ is denoted by black tick marks. An additional phase is present but could not be fit from the powder data.

References:

1. C. Hasselgren, S. Jagner, Dirubidium *catena*-poly[dichloro-argentate(I)-μ-chloro]., *Acta Cryst.*, 1999, **C55**, 1208.
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