
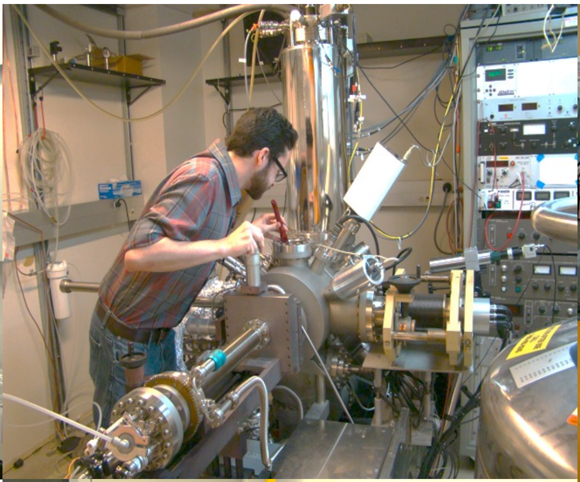

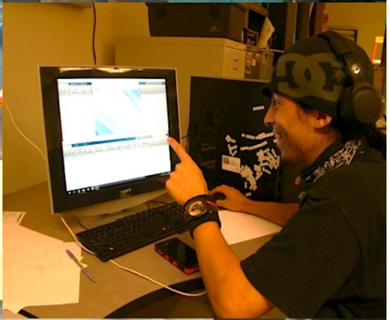

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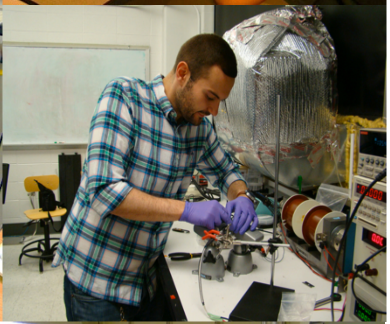


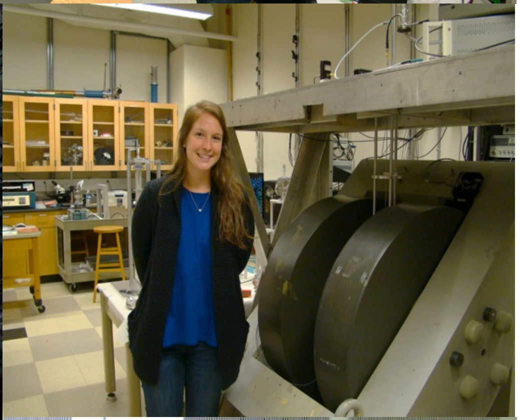
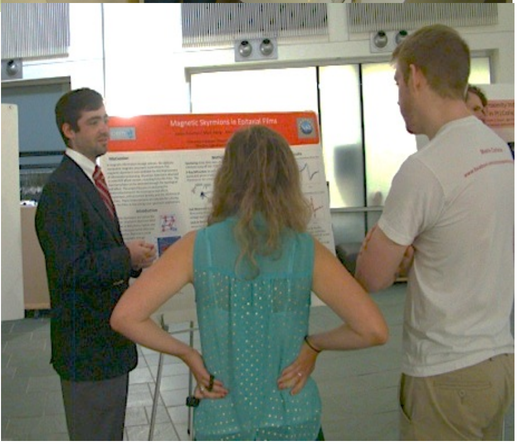

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ABSTRACT

The synthesis of the double perovskites $Cs_2AgBiCl_6$, $Cs_2AgInCl_6$, $Cs_2NaInCl_6$ from solution methods have been analyzed using x-ray diffractions. In order to understand what byproducts are being made in the complex synthesis of the double perovskites, multiple ternary phase diagrams have been constructed with each point representing a compound synthesized by either solution or solid state grinding methods. The ternary phase diagrams vary by halide X=Cl, Br, I and by the M^{3+} =Bi, Sb, In site with the constant AgX and CsX component. The phase diagrams help organize the synthesis data for any future research done on lead free halide double perovskites. Multiple synthesis attempts were made on the Cs2AgBiI6 using different reagents and solvents, but the XRD is not conclusive to declare the perovskite form. The Cl-Bi and Br-Bi are complete phase diagrams, but the I-Bi diagram products indicate the system is not yet thermodynamically stable. Synthesis of $AgBiBr_4$, Cs_3BiBr_6, $AgBi_2I_7$ have no literature cited crystal structure and their x-ray crystallography images show promise for solving their structures.

Background and Introduction

In the past few years alone, the scientific community has seen a great spike in metal-halide perovskite research. What initially sparked the interest in these perovskites was their potential ability within photovoltaic technology. However, perovskites have not quite reached the efficiency of the today's dominating silicon technologies. The perovskite takes on the crystalized ABX_3 structure, with an organic cation A site, B the metal cation, and X being the halide anion. Lead-halide perovskites, PbX_3, have been greatly analyzed because of the potential ability in LEDs and solar energy devices[1]. However, while their efficiency and spectra potential continue to amaze the scientific community, mass producing anything with lead brings up many negative environmental questions. As lead is toxic, people are rapidly trying to remove lead in all current and future products.

Research has begun on using lead alternatives like Sn2+ and Ti, however stability is a common probably in the synthesis of these perovskites where they disintegrate quickly over time when exposed to air[2]. Due to the limiting factors of stability of these lead perovskites and the need of a 2+ cation, it was found that by expanding the search from the previous ternary ABX_3 to quaternary double perovskites may help improve the search for a viable lead alternative. The double perovskite contains the face cubic crystal structure, but expands the unit cell taking on a form of $A_2M^{+}M^{3+}X_6$ where you can use a 1+ and 3+ ions. For example, using cooper, silver, bismuth, or antimony as the M^{3+} site and silver as the M^{+} site[3,4].

As followed in the continuation of McClure et. al[4], the double perovskites sometimes produce unwanted irregular 3-2-9 impurities that take on the $A_3M_2^{3+}X_9$, which negatively effects the stability of the desired product. In addition, the method of synthesis of such double perovskites seems to not be fully clear on why hypophosphorous acid, H_3PO_4 is necessary. In order to analyze what reagents are at play, ternary phase diagrams can be used to help bring clarity into the synthesis of the double perovskites. In double halide perovskites it has been suggested that as you move down the halide groups the perovskites synthesize have better band gap properties, in other words absorbing more light. $Cs_2AgBiCl_6$ is yellow, and $Cs_2AgBiBr_6$ is orange, and the iodine perovskite therefore would be red/black color absorbing more light in the visible spectrum. However, iodine double perovskites have not been able to be successfully synthesize. Therefore, by creating a phase diagram the includes the iodine axis this will also help understand what might be the factors are contributing to the challenges of its synthesis, and how it's phase diagram compares to the other halide phase diagrams.

Ultimately, these diagrams will help understand all the unwanted byproducts, or if there is any undiscovered combination of reagents forming that can be used as a tool for figuring out other combinations of lead free double perovskites that may be able to be synthesized. The phase diagrams will also produce a way of coming up with new chemical formula combinations in the synthetic attempt to make the double perovskites, when certain reagents are less financially practical or more challenging to work with. Phase diagrams give a comprehensive understanding of chemical systems, with different pressures and temperatures. However, the phase diagrams described in this paper will have zero degrees of freedom, meaning pressure and temperature will remain constant. Each line drawn on the phase diagrams between two points, points are synthesized products, describes a composition of the two products or the points the line is between. And moving off the line into the empty space of the phase diagram would describe a composition of multiple products[5]. In summary, phase diagrams help show;

- What factors contribute to the challenges of its synthesis
- How the halide phase diagrams differ from one another
- All the unwanted byproducts
- Relative amounts and ratios of each of the elements
- Methods of creating the purist compounds
- A tool for using new chemical formula combinations
- A comparison across the different halide perovskites products

II. Methods

There were two methods used for the synthesis of compounds made, solid state grinding and solution method. For the synthesis of all double perovskites $Cs_2AgBiCl_6$, $Cs_2AgInCl_6$, $Cs_2NaInCl_6$ $Cs_2AgSbCl_6$, or any compound that will fall within the center of the phase diagram the solution method was used. In general, for any compound made which would lie on the axis that included the M^{3+} site, ie; Bi, Sb, In which includes always a dominant 3-2-9 irregular perovskites $Cs_3Bi_2Cl_6$, $Cs_3Bi_2Br_6$ $Cs_3Sb_2Cl_6$was synthesized by solution method.

The bismuth containing compounds were dissolved in 10mL of 12.1M HCl that was added to a 50mL beaker heated to 100°C, then using the correct 2:1:1 molar ratio the solid Bi_2O_3 (≥ 99.0%, J.T Baker) was added to the beaker with constant stirring till dissolved. Then the proper amount of the AgCl and AgBr was added to the beaker, wait about 30 minutes till the majority of reagent dissolves. The AgCl and AgBr were precipitated from an in house prepared aqueous solution of $AgNO_3$ (99.9+%, Alfa Aesar) and NaCl (ACS Reagent, GFS Chemicals) or KBr (99+%, Alfa Aesar). Lastly, the CsCl (≥ 99.0%, Aldrich) and CsBr, was prepared in house by reacting Cs2CO$_3$ (99+%, Strem Chemicals) with HBr (Fluka, ≥ 48%). Upon the addition of CsX to the hot solutions visually the precipitant formed in all double perovskites synthesized and 3-2-9s. All solution samples were collected on filter paper and washed with ether.

The antimony containing compounds were synthesized in the same method as Bismuth but using Sb_2O_3 (≥ 99.0%, Aldrich). The indium containing compounds were synthesized using In_2O_3 (≥ 99.0%, Aldrich) and 10 mL of 6 M HCl then continuing the same methods as the bismuth. Any other compounds formed using the M^{3+} site used solution method as described above with the only difference marking the change in concentrated HCl depending on Bi, Sb, or In [$CsInCl_4$, Ag_3InCl_6, $AgBiC_4$]. The Indium compounds were synthesized a second time using a glove bag with nitrogen air during the grinding of the products in the mortar and pestle. However, products still took on water during XRD preparation.

All solution method compounds made were stirred to evaporated dryness and were left overnight. The samples were then grinded on an agate mortar and pestle for 20 minutes and prepared on pmma acrylic slides.

50% solution of H_3PO_3 was added to a separate batch of $Cs_2AgBiCl_6$ and $Cs_2AgSbCl_6$, and the $Cs_3Bi_2Cl_6$ and $Cs_3Sb_2Cl_6$ at room temperature, along with the different reagents to test the dissolving properties of phosphoric acid. First test tubes with small unmeasured amount were used as a visual test of dissolution. In a 50mL beaker about 1 gram of the above double perovskites and 3-2-9 were stirred with the acid and then drained, and then vacuum filtrated and prepared for analysis by grinding and then prepped on a stainless steel x-ray slide.

All compounds synthesized the lie on the AgX and CsX of the phase diagram were made using solid state grinding methods. Using varying molar ratios, the in house preparations of AgCl, AgBr, and AgI, which was made with $AgNO_3$ (99.9+%, Alfa Aesar) and KI (ACS Reagent, GFS Chemicals). CsCl (≥ 99.0%, Aldrich), and CsBr, and CsI made with the Cs2CO_3 (99+%, Strem Chemicals) with and HIO_3. The regents were grinded together with an agate mortar and pestle till a loose powder form, about 15 minutes before heating. Then the products were placed in an alumina crucible for their heating in a box furnace in air at 200^{o}C for 72 hr. It was found that in order to achieve the most phase pure version of $CsAgCl_2$ sample needed to be heated at 400^{o}C for 10 hr.

In addition, while attempting to make a low temperature unreported literature product of $CsAgI_2$ and the varied molar ratio product of $CsAg_{3/2}I_{2/5}$ products was synthesized multiple times at different temperatures and times 72 hr 200^{o}C, 12 hr 200^{o}C, 10 hr 100^{o}C. All products were then re grinded for 20 minutes and prepared on are pmma acrylic slides for analysis.

$Cs_3Bi_2Cl_6$ and Cs_3BiCl_5 was synthesized using solid state grinding techniques with the correct molar ratio of CsCl and the prepared in house $Cs_3Bi_2Cl_9$.

Cs_2AgBiI_9 was synthesized with three different reagents combinations. One from the in house preparation of Cs_2AgI_3 and BiI_3 that was grinded in a solid state reaction and heated for 18hr and 150^{0}C. And synthesized with in house $CsAg_2I_3$, CsI, and BiI_3 with the same procedure.

$Cs_2AgI_3 + BiI_3 \rightarrow Cs_2AgBiI_9$

$1/2\ CsAg_2I_3 + 3/2\ CsI + BiI_3 \rightarrow Cs_2AgBiI_9$

Then, upon heating one batch was separated for a 72hr heating cycle while the other was mixed with 4mL of hydroiodate acid and 1mL of Hypophosphorous Acid (50wt. % H_20, Sigma Aldrich), and the other was heated on a stir plate with 3mL of H_3PO_2.

The third method included grinding together the AgI, BI3, and CsI, reagents with three different solvents, methanol (99+%, Fischer Chemical), ethanol (200 proof, Decon Lab) and acetonitrile (99+%, Fischer Chemical) in a beaker heated to 150^{0}C 10mL. The appropriate solvent was added and stirred, color change can be seen right away and heated to dryness with initial XRDs. Then an addition of 3mL of H_3PO_2 acid and 5mL of methanol was re-added to the methanol solvent attempt, but could not be heated to dryness. The ethanol solvent attempt was then heated to 350^{o}C for 48hr and grinded for XRD. The acetonitrile compound was heated at 150^{0}C for 48hr and grinded again for XRD preparation. All slides used are pmma acrylic.

X-ray powder diffraction (XRPD) data was collected on a Rigaku Miniflex II benchtop diffractometer (30kV 15mA, sealed Cu X-ray tube) with a NaI scintillation detector. For the products synthesized by McClure et. al[4] [$Cs_2AgBiBr_6$, $Cs_3Bi_2Br_9$, $Cs_3Bi_2I_9$] used x-ray powder diffraction (XRPD) collected on a Bruker D8 powder diffractometer (40 kV, 50 mA, sealed Cu X-ray tube) equipped with an incident beam Ge 111 monochromator and Lynx Eye position sensitive detector.

Refinements of laboratory XRD data was carried out using TOPAS Academic software package with both Pawley and Rietveld refining to analyze the purity, crystal structure, and phase identification.

II. Results and Discussion

Each section includes a theoretical phase diagram constructed by using points that have been stated in literature to exist. Each ternary phase diagram has zero degrees of freedom where pressure and temperature are being kept constant.

Key of phase diagrams

⬛ Successful synthesis of desired product

🟨 Successful synthesis of double perovskite

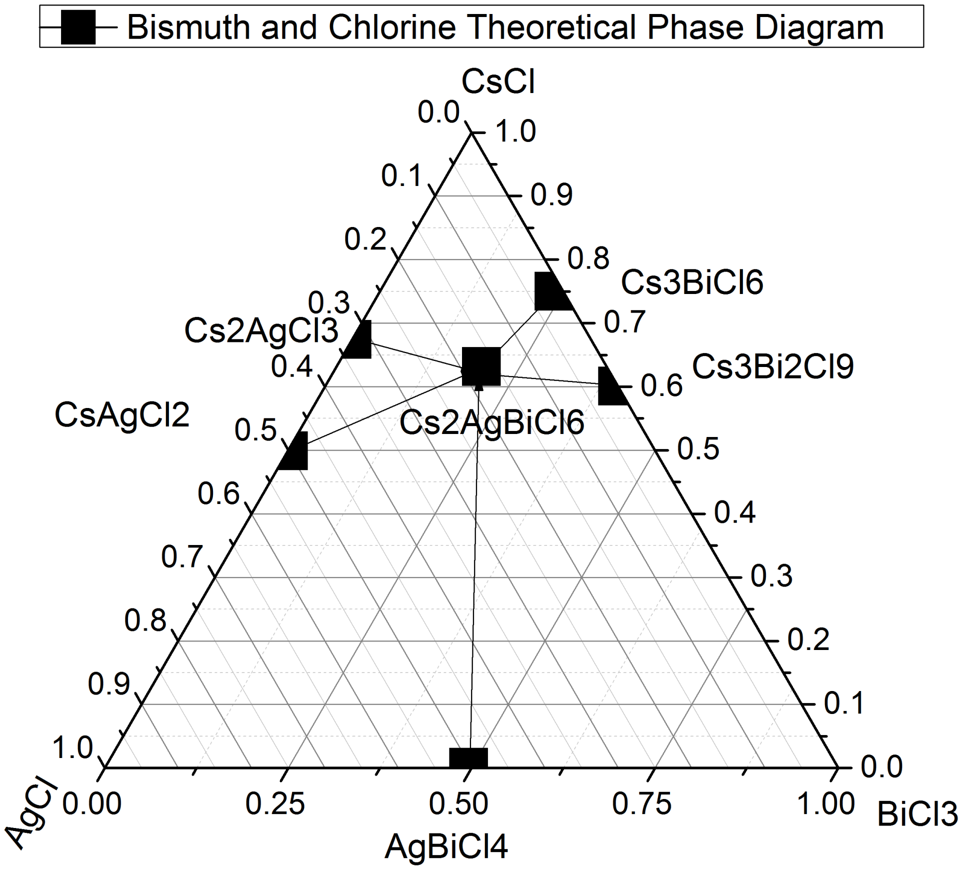
🟦 Successful synthesis of literature reported product but no detail crystal structure reported (only includes lattice parameters)

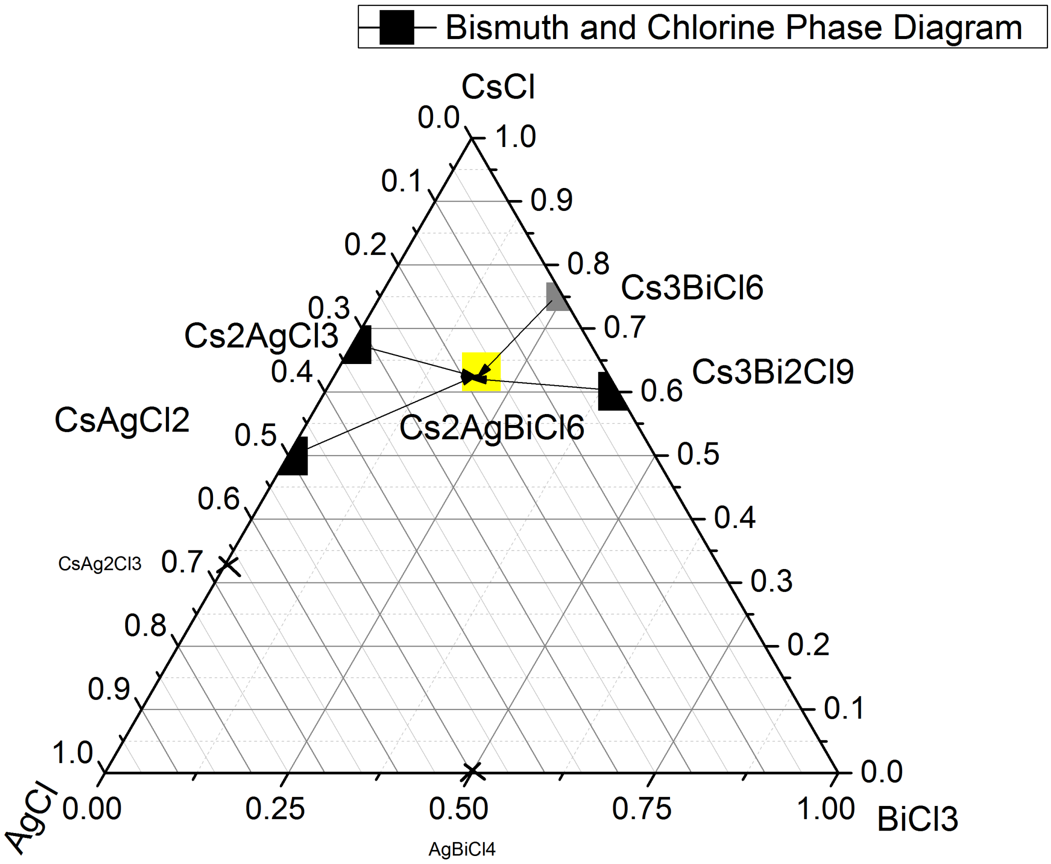
▩ Successful synthesis of literature reported product, but includes a mixture of two products. Not thermodynamically stable

X Unsuccessful attempt at product with synthesis methods used or is the compositional mixture of the axis of the phase diagram

X XRD does not produce a sufficient pattern to declare perovskite form is present

Chlorine-Bismuth Results





Difference Summary of Theoretical to Experimental Diagram

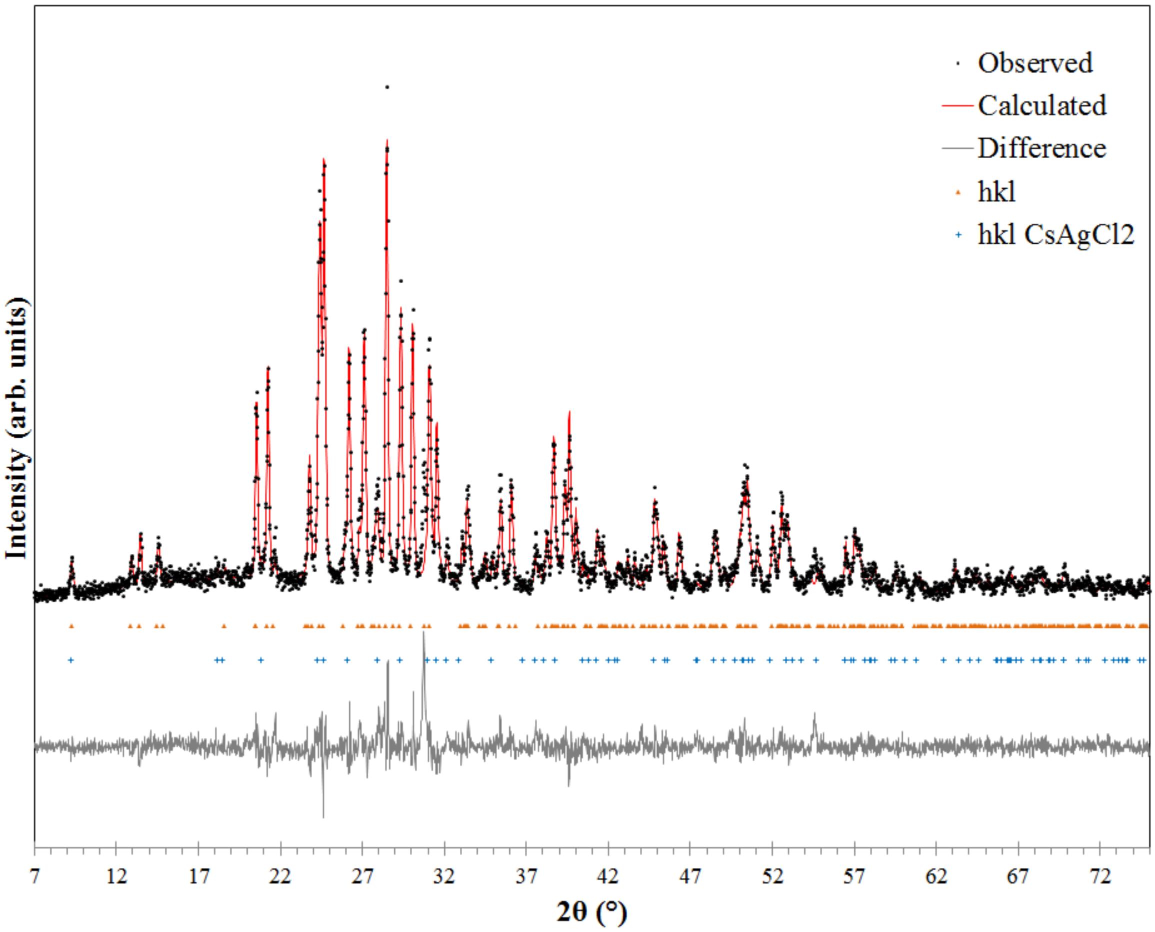
The phase diagram constructed in the chlorine includes three differences.

1. The product $AgBiCl_4$ was not able to be successful synthesized due to its hygroscopic properties. The product was a mushy whitish purple color and was resynthesized multiple times with different heating techniques to try to get a dry powder for XRD preparation, but no successful synthesis was made.
2. The $CsAg_2Cl_3$ point included a compositional mixture of $CsAgCl_2$ and AgCl which would be expected by the phase diagram.
3. Cs_3BiCl_6 was not a pure compound and XRD pattern shows that 3-2-9 dominated the product, but some of the desired product as probably made. May not be a thermodynamic equilibrium.

XRD Chlorine-Bismuth Results

Product	Space group	Rwp

[6]Cs_2AgCl_3 *(includes $CsAgCl_2$ impurity)	Pnma #62	15.66



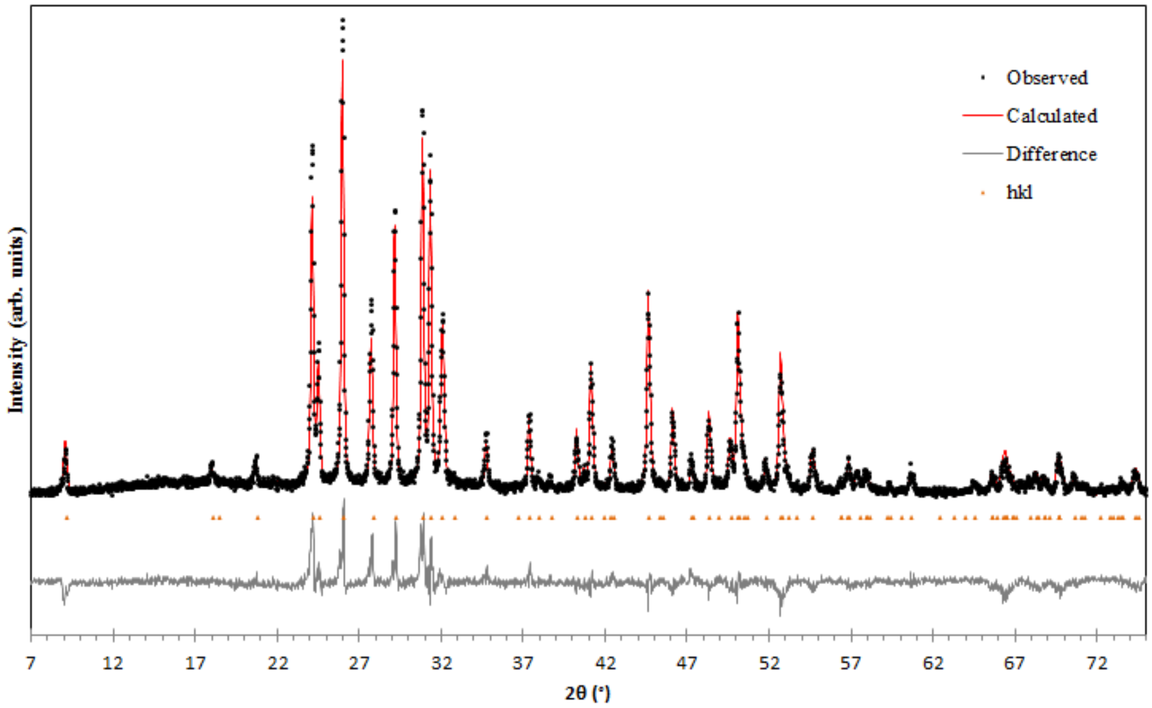
Cell Parameters	Å
a	13.2104
b	4.5528
c	13.7611

Site	Wyckoff site	x	y	z	Beq
Ag_1	4c	0.2514	¼	0.3014	4.9976
Cs_1	4c	0.1703	¼	0.0186	3.5104
Cs_2	4c	0.0121	¼	0.6730	3.5104
Cl_1	4c	0.1296	¼	0.4515	3.3696
Cl_2	4c	0.4474	¼	0.3613	3.3696
Cl_3	4c	0.2798	¼	0.7060	3.3696

[redacted]

$^6CsAgCl_2$	Cmcm #63	15.54

Successful synthesis, but CsAgCl2 has a minor presence is product

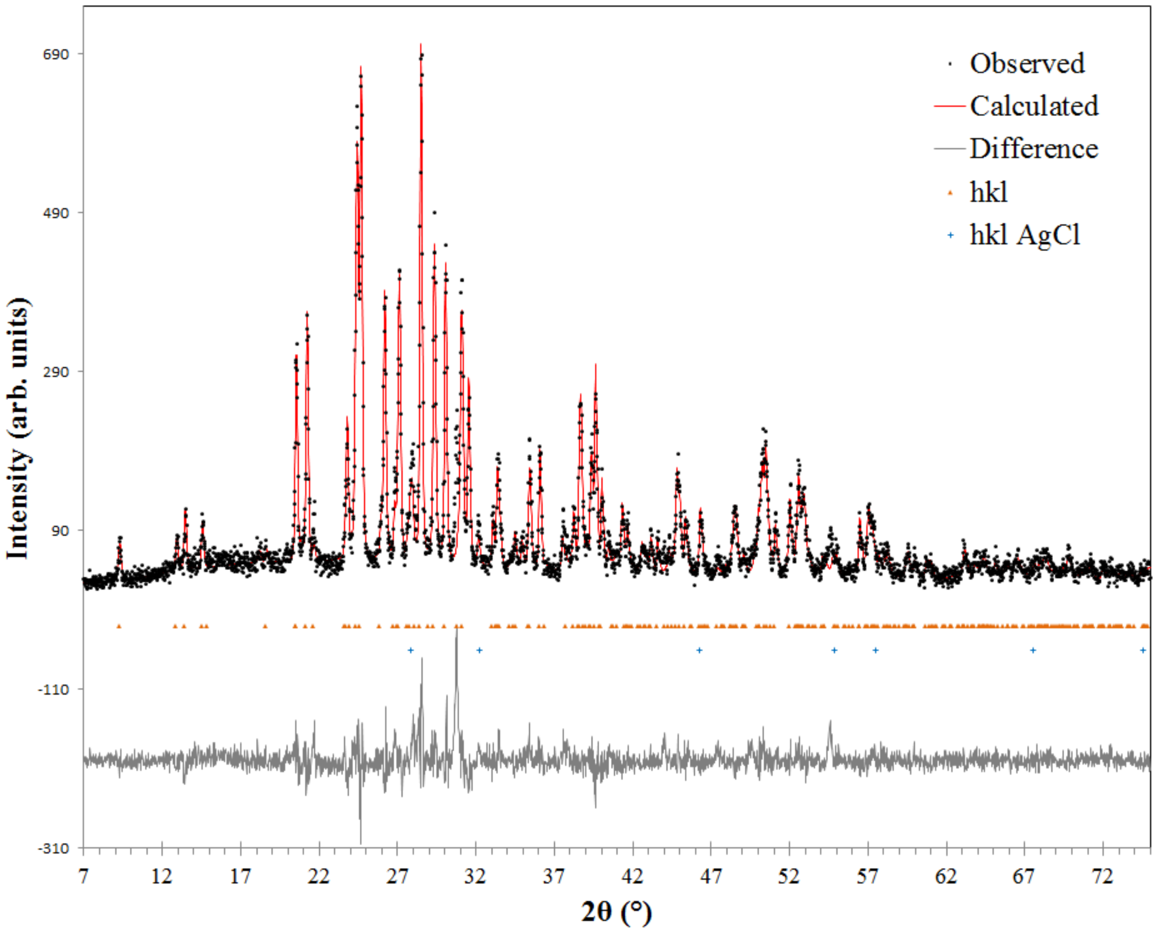


Cell Parameters	Å
a	4.3712
b	19.1764
c	5.6804

Site	Wyckoff site	x	y	z	Beq
Ag_1	4c	0.0000	0.4176	¼	3.2036
Cs_1	4c	0.0000	0.1988	¼	4.0099
Cl_1	4c	0.0000	0.7770	¼	3.6987
Cl_2	4c	0.0000	0.0676	¼	3.3696

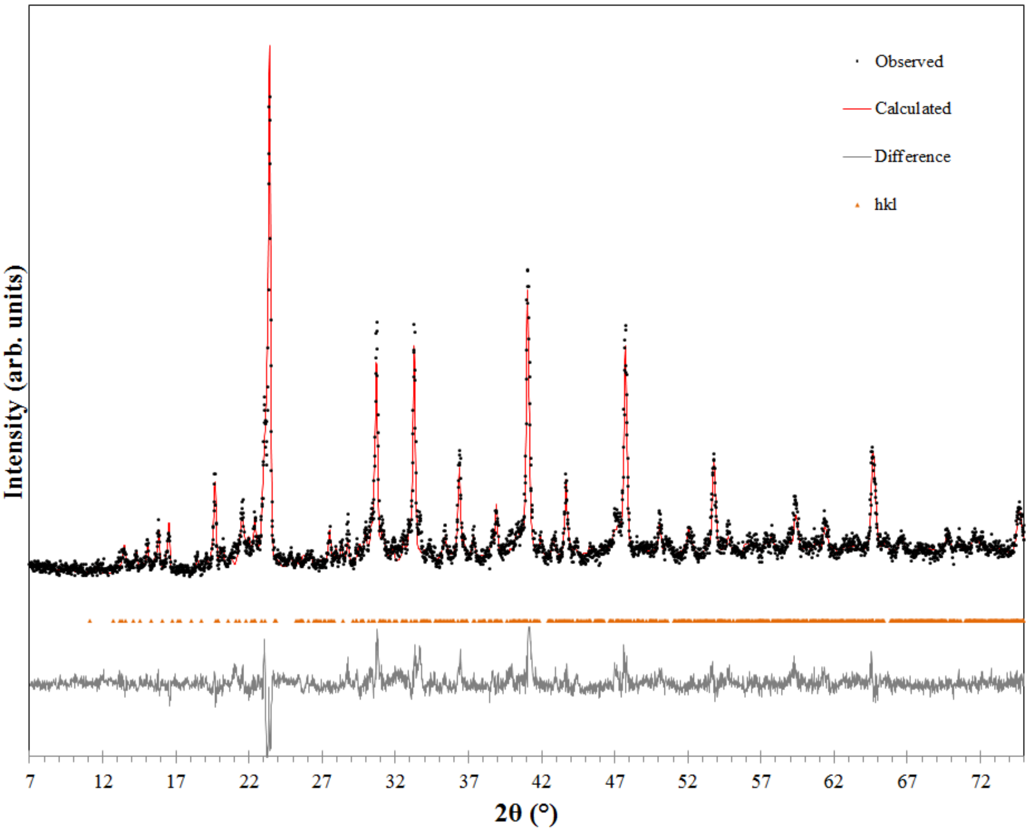
[redacted] Successful synthesis

$CsAg_2Cl_3$ mixture of $CsAgCl_2$ and AgCl



X Product is a compositional mixture between the AgCl point and CsAgCl2

$^{78}Cs_3BiCl_6$ *(Dominant Cs_3BiCl_9)	C12/c1 #15	15.54

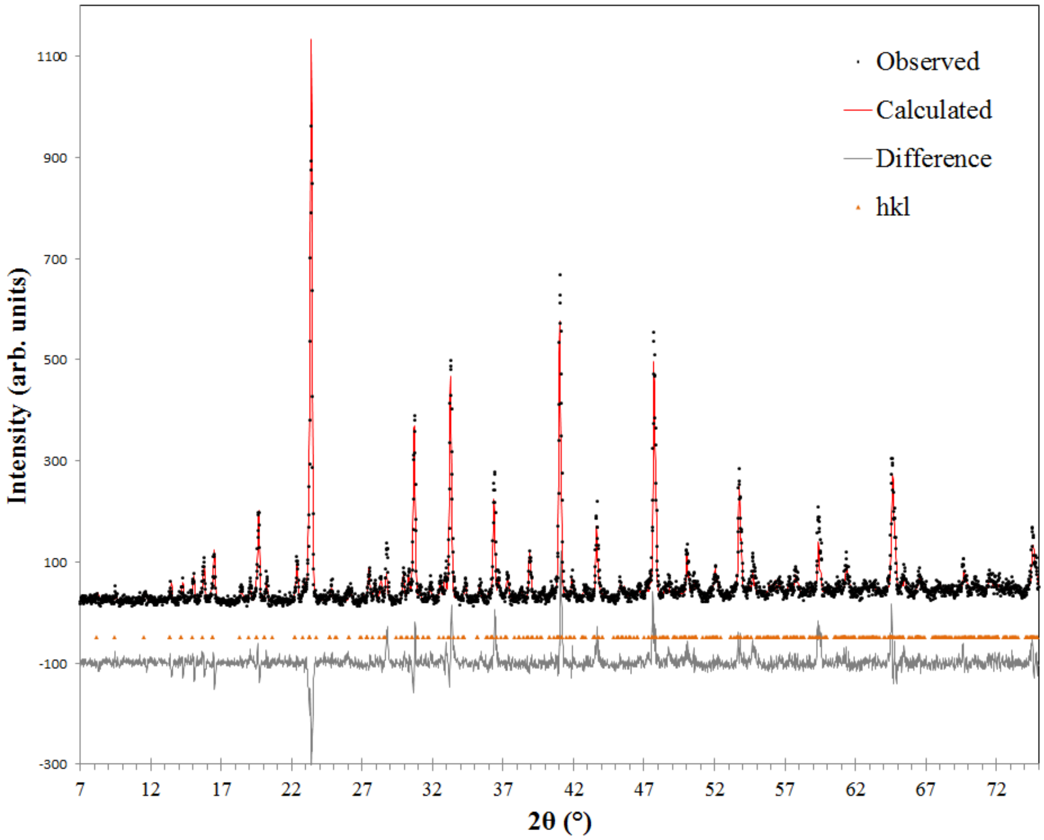


Cell Parameters	Å
a	26.8906
b	8.2985
c	13.1646
al	90
be	99.9357
ga	90

Site	Wyckoff site	x	y	z	Beq
Bi_1	4c	¼	¼	0.0000	-5.0937
Bi_1	4e	0.0000	0.2043	¼	-5.0937
Cs_1	8f	0.4781	0.2114	0.0615	-5.0937
Cs_2	8f	0.1584	0.2494	0.2953	-10
Cs_3	8f	0.3357	0.1908	0.3445	-10
Cl_1	8f	0.2393	0.3546	0.1571	-10
Cl_2	8f	0.1641	0.2732	0.0140	-10
Cl_3	8f	0.3991	0.1413	0.0431	-10
Cl_4	8f	0.0867	0.6799	0.2604	-10
Cl_5	8f	0.0633	0.2870	0.4114	-10
Cl_6	8f	-0.0083	0.0704	0.6150	-10

■ Mixture of two products may not be at thermodynamic equilibrium

[4]$Cs_3Bi_2Cl_9$	Pnma #62	29.91



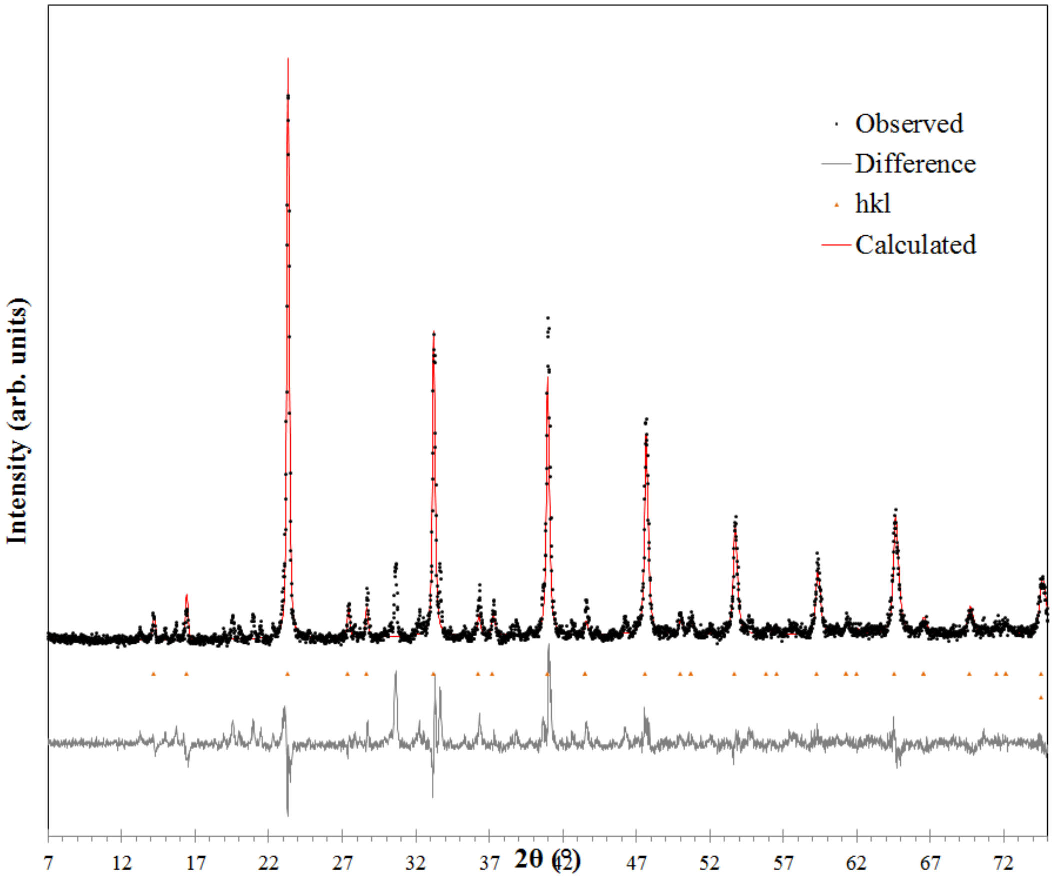
Cell Parameters	Å
a	18.6899
b	7.6259
c	13.2378

Site	Wyckoff site	x	y	z	Beq
Bi_1	4c	0.0004	¼	0.2611	0.5090
Bi_2	4c	0.6824	¼	0.5846	0.4390
Cs_1	4c	0.4169	¼	0.5910	2.6980
Cs_2	4c	0.2501	¼	0.2499	1.8930
Cs_3	4c	0.0876	¼	0.5843	1.6890
Cl_1	4c	0.0909	¼	0.0922	2.5320
Cl_2	4c	0.2577	¼	0.7453	1.2190
Cl_3	4c	0.4173	¼	0.0758	1.9780
Cl_4	8d	0.0764	-0.0128	0.3482	3.1490
Cl_5	8d	0.2538	-0.0145	0.0035	3.1020
Cl_6	8d	0.4150	0.4884	0.3392	4.1600

Successful synthesis

[redacted]

$^{4}Cs_2AgBiCl_6$	Fm-3m #225	23.17

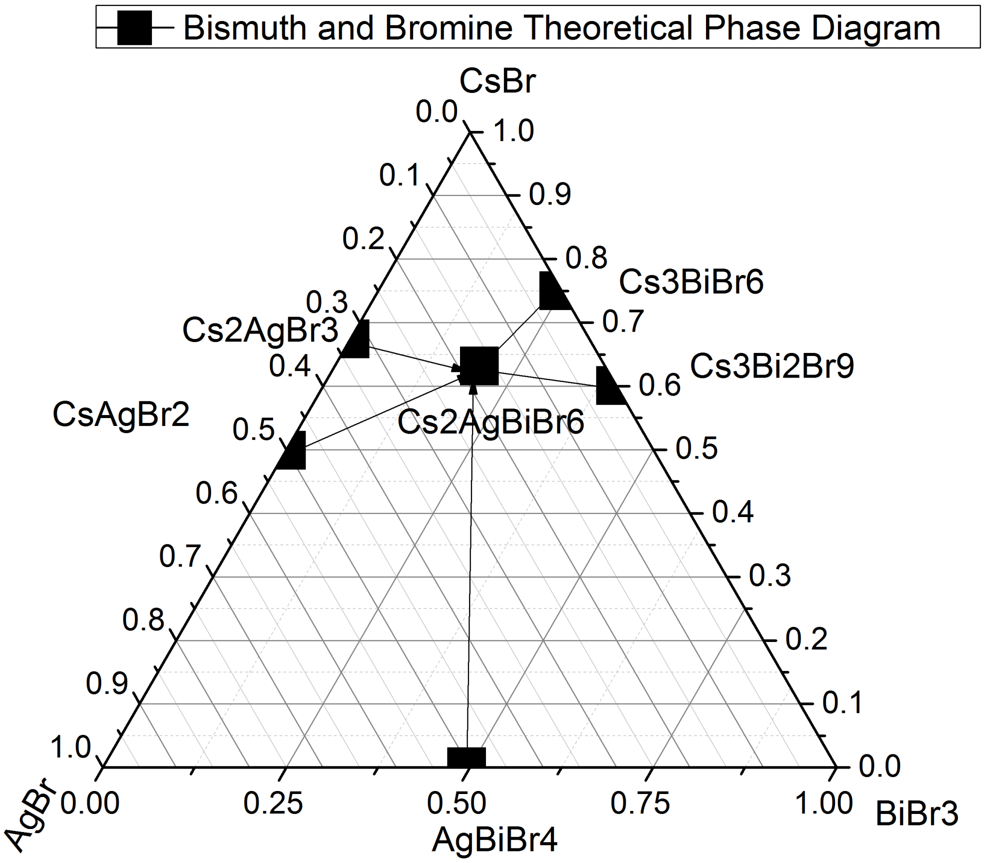


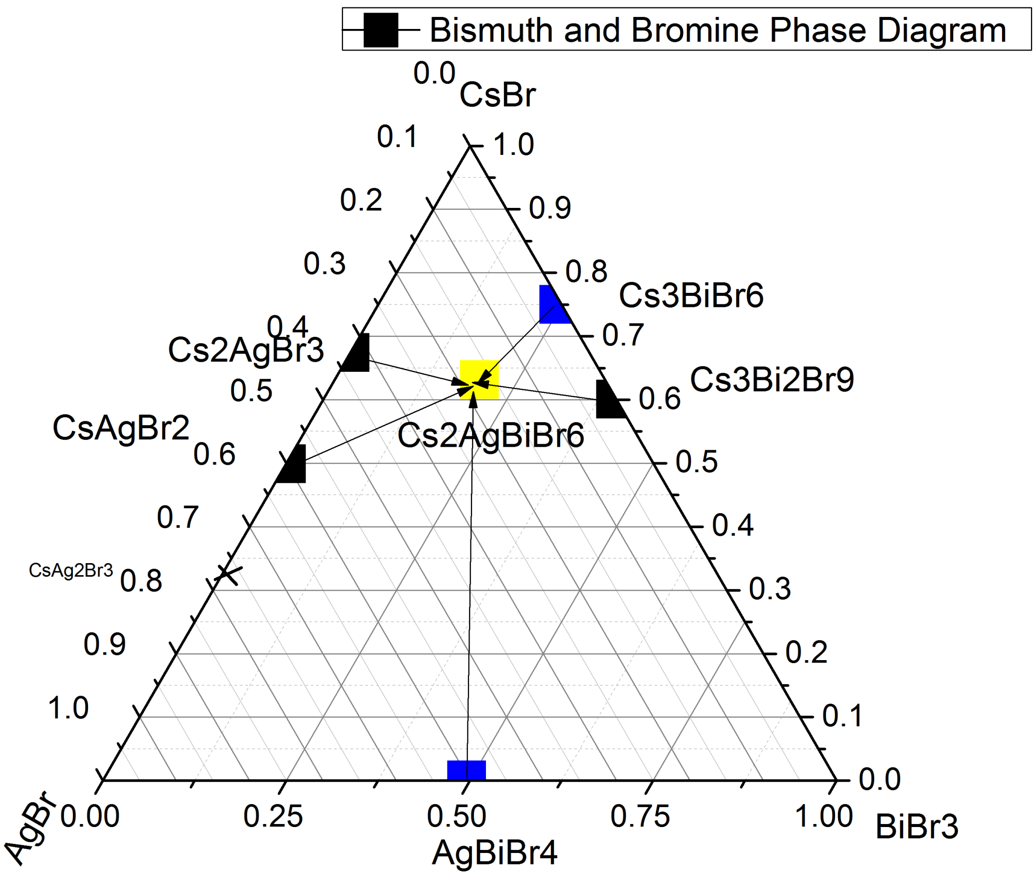
Cell Parameters	Å
a	10.7853
b	10.7853
c	10.7853

Site	Wyckoff site	x	y	z	Beq
Ag_1	4a	0.0000	0.0000	0.0000	0.9094
Bi_1	4b	½	0.0000	0.0000	-2.1852
Cs_1	8c	¼	¼	¼	-0.7178
Cl_1	24e	0.2432	0.0000	0.0000	-1.6924

Successful synthesis of double perovskite, adding H_3PO_2 acid is necessary to dissolve the 3-2-9 and to give the purist XRD, see procedure

Bromine-Bismuth Results


Bismuth and Bromine Theoretical Phase Diagram
CsBr
AgBr
BiBr3
AgBiBr4
Cs3BiBr6
Cs3Bi2Br9
Cs2AgBr3
CsAgBr2
Cs2AgBiBr6
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0.00
0.25
0.50
0.75
1.00



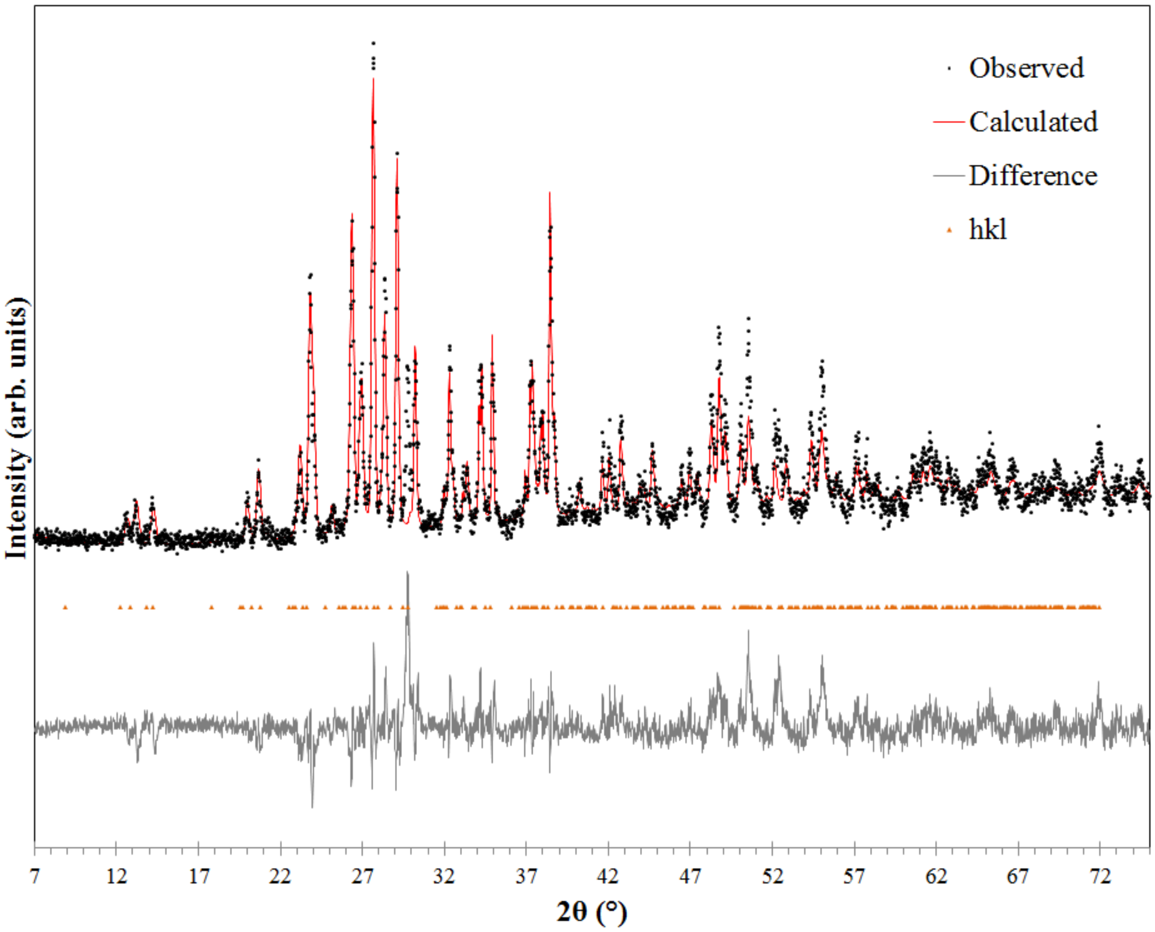
Difference Summary of Theoretical to Experimental Diagram

1. $CsAg_2Br_3$ product does not exist but the point is the expected ratio of composition of AgBr and $CsAgBr_2$
2. $AgBiBr_4$ is a curry yellow compound that has been reported in literature but no detail crystal structure reported
3. Cs_3BiBr_6 is bright yellow compound that has been reported in literature but no detail crystal structure reported

XRD Results of Bromine-Bismuth Results

Product	Space group	Rwp

[6]Cs_2AgBr_3	Pnma #62	17.99

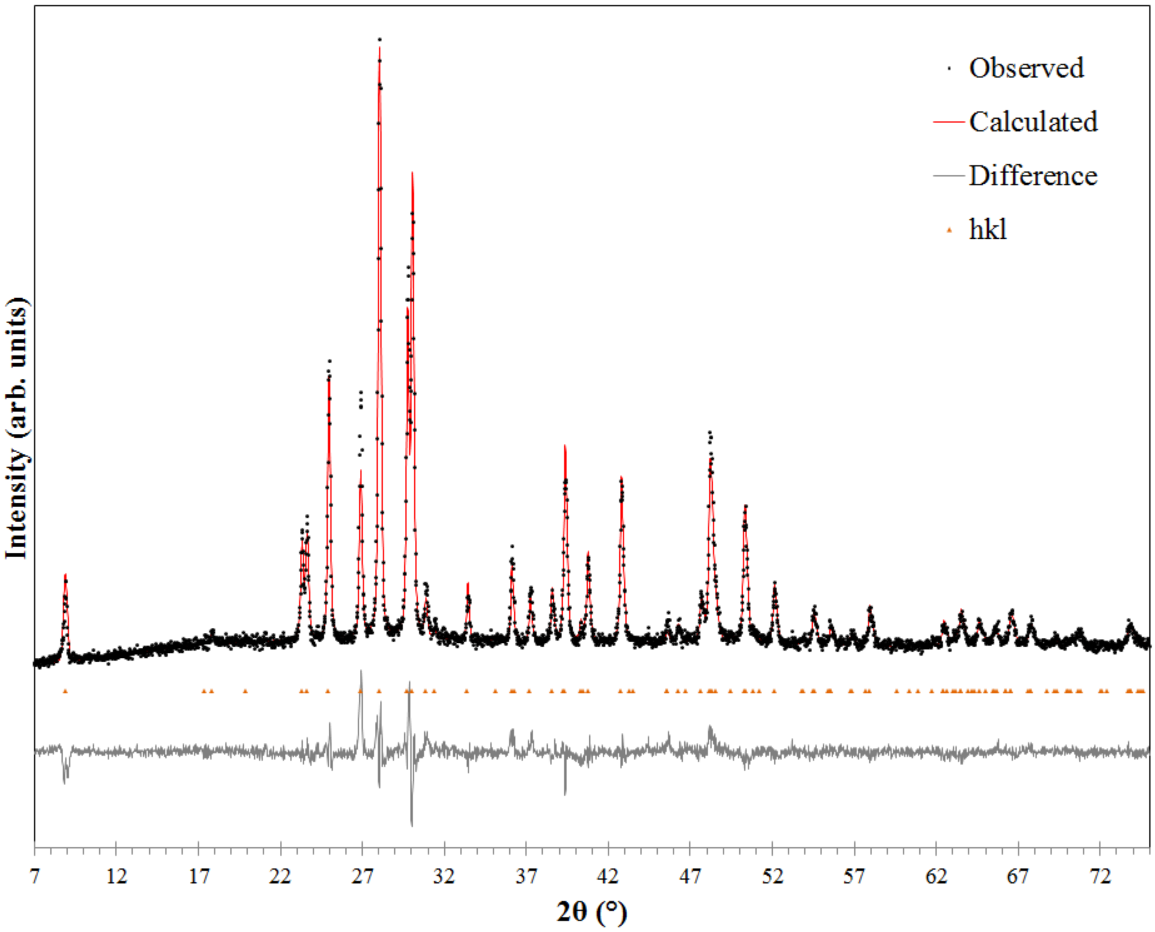


Cell Parameters	Å
a	13.7671
b	4.7222
c	14.3745

Site	Wyckoff site	x	y	z	Beq
Ag_1	4c	0.2497	¼	0.2999	3.8000
Cs_1	4c	0.1733	¼	0.0171	3.6500
Cs_2	4c	0.1273	¼	0.6510	3.6500
Br_1	4c	0.1299	¼	0.4549	4
Br_2	4c	0.4470	¼	0.3623	4
Br_3	4c	0.2776	¼	0.7100	4

■ Successful synthesis

[6]CsAgBr$_2$	Cmcm #63	10.19

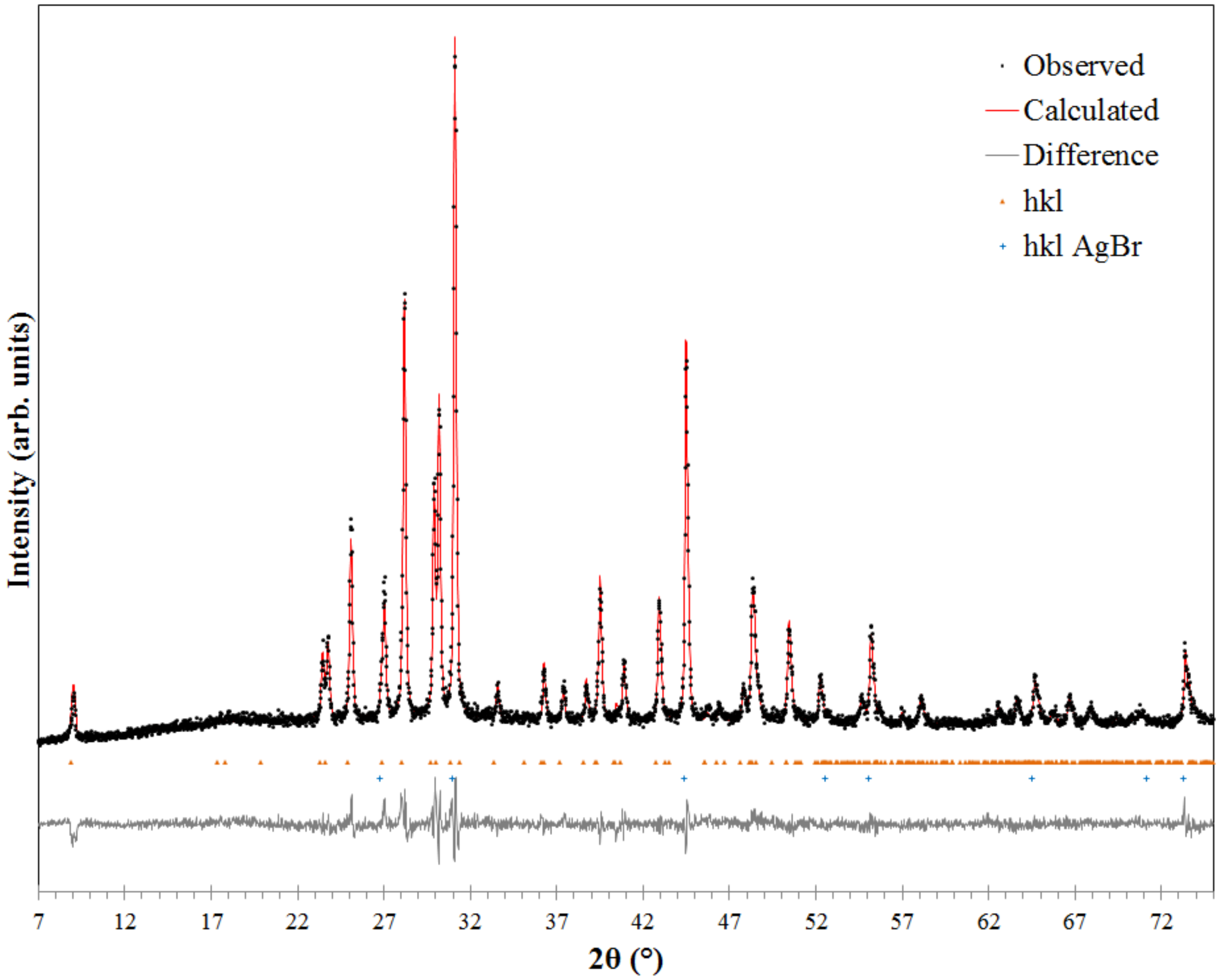


Cell Parameters	Å
a	4.5723
b	19.8795
c	5.9435

Site	Wyckoff site	x	y	z	Beq
Ag_1	4c	0.0000	0.2006	¼	4.2439
Cs_1	4c	0.0000	0.4184	¼	3.4133
Br_1	4c	0.0000	0.7732	¼	3.3139
Br_2	4c	0.0000	0.0664	¼	3.3139

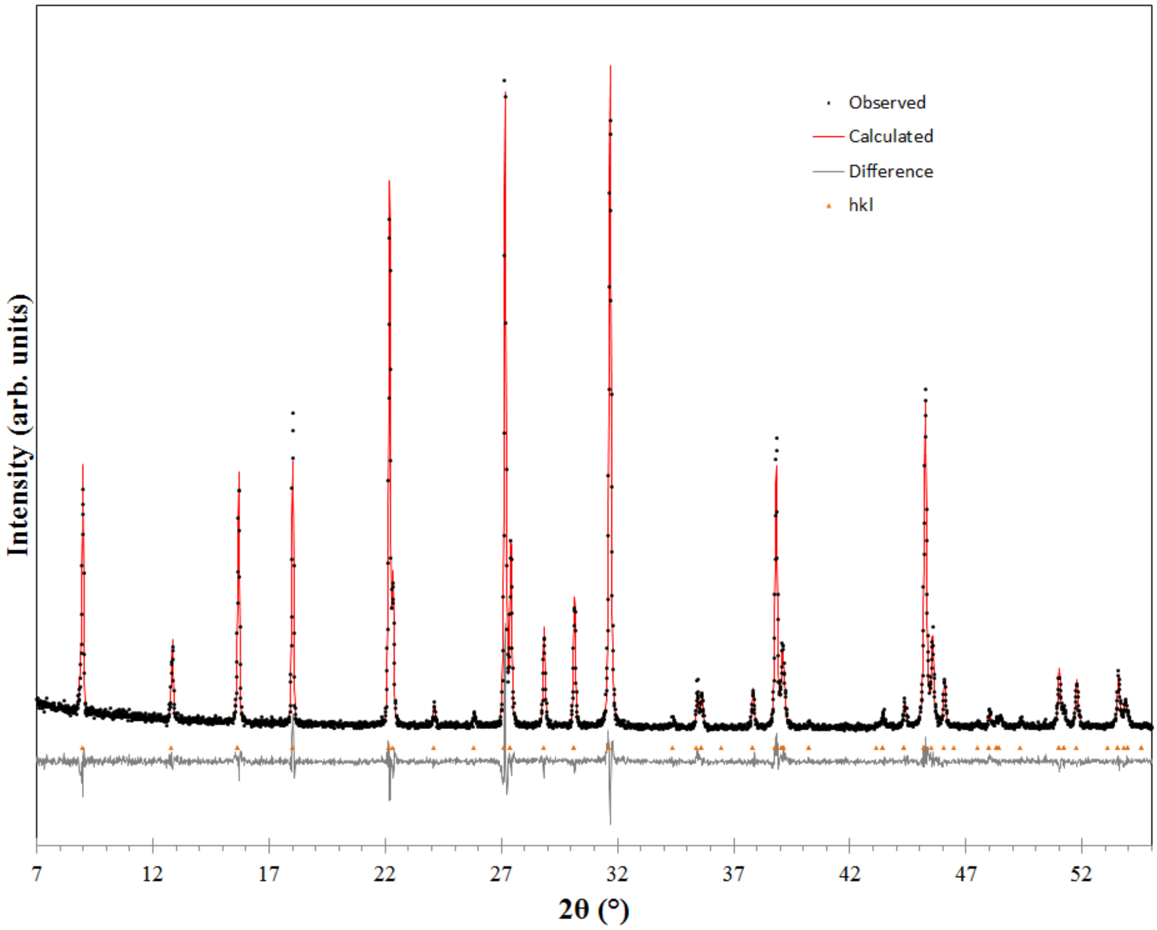
■ Successful synthesis

$CsAg_2Br_3$ a mixture of $CsAgBr_2$ and AgBr



X Product is a compositional mixture of $CsAgB_2$ and AgBr

[4,9]$Cs_3Bi_2Br_9$ (Bruker D8)	Pnma #62	29.91

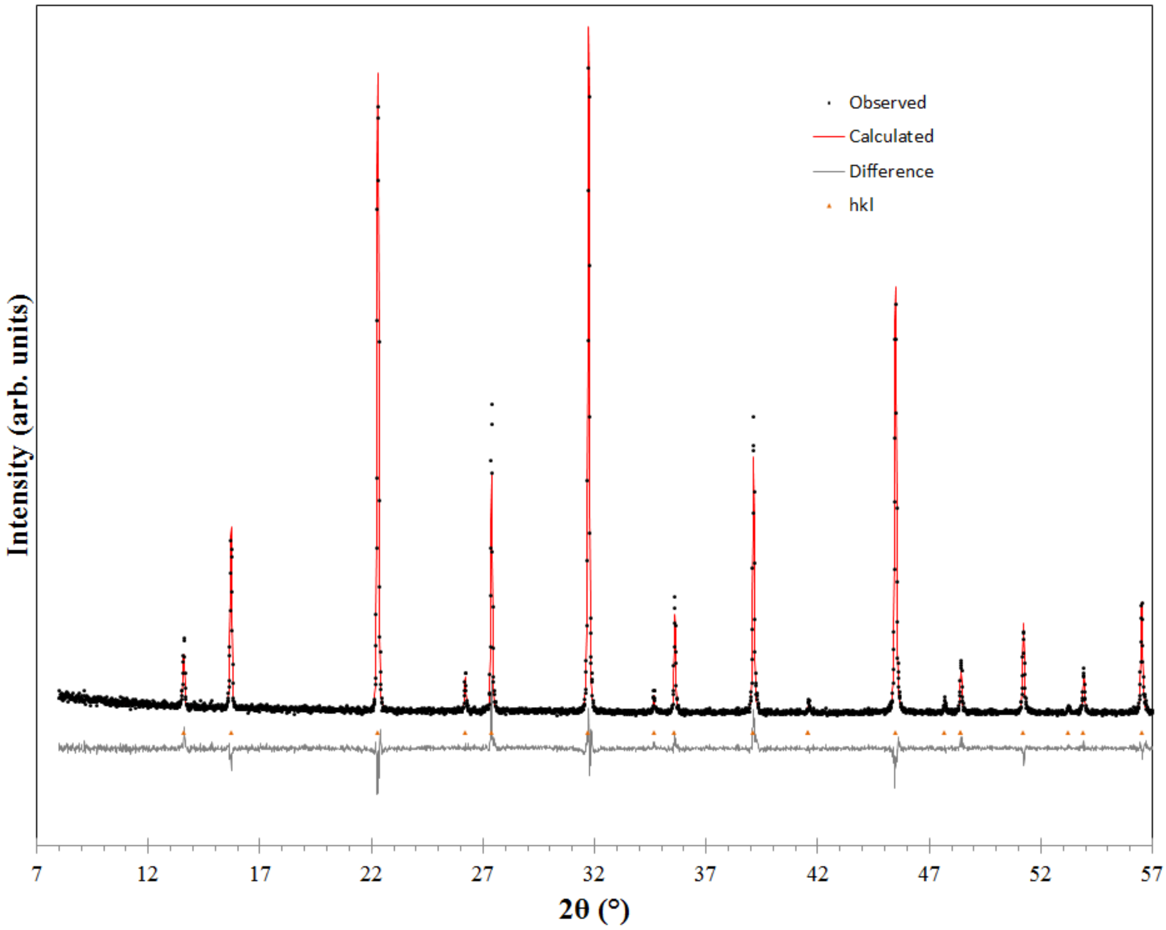


Cell Parameters	Å
a	7.9614
b	7.9614
c	9.8480

Site	Wyckoff site	x	y	z	Beq
Cs_1	1a	0.0000	0.0000	0.0000	3.5069
Cs_1	2d	1/3	2/3	0.6668	3.5069
Bi_1	2d	1/3	2/3	0.1932	0.9935
Br_1	3e	½	0.0000	0.0000	3.3082
Br_2	6i	0.1664	0.8336	0.3398	3.3082

■ Successful synthesis

[4]$Cs_2AgBiBr_6$ (Bruker D8)	Fm-3m #225	20.96

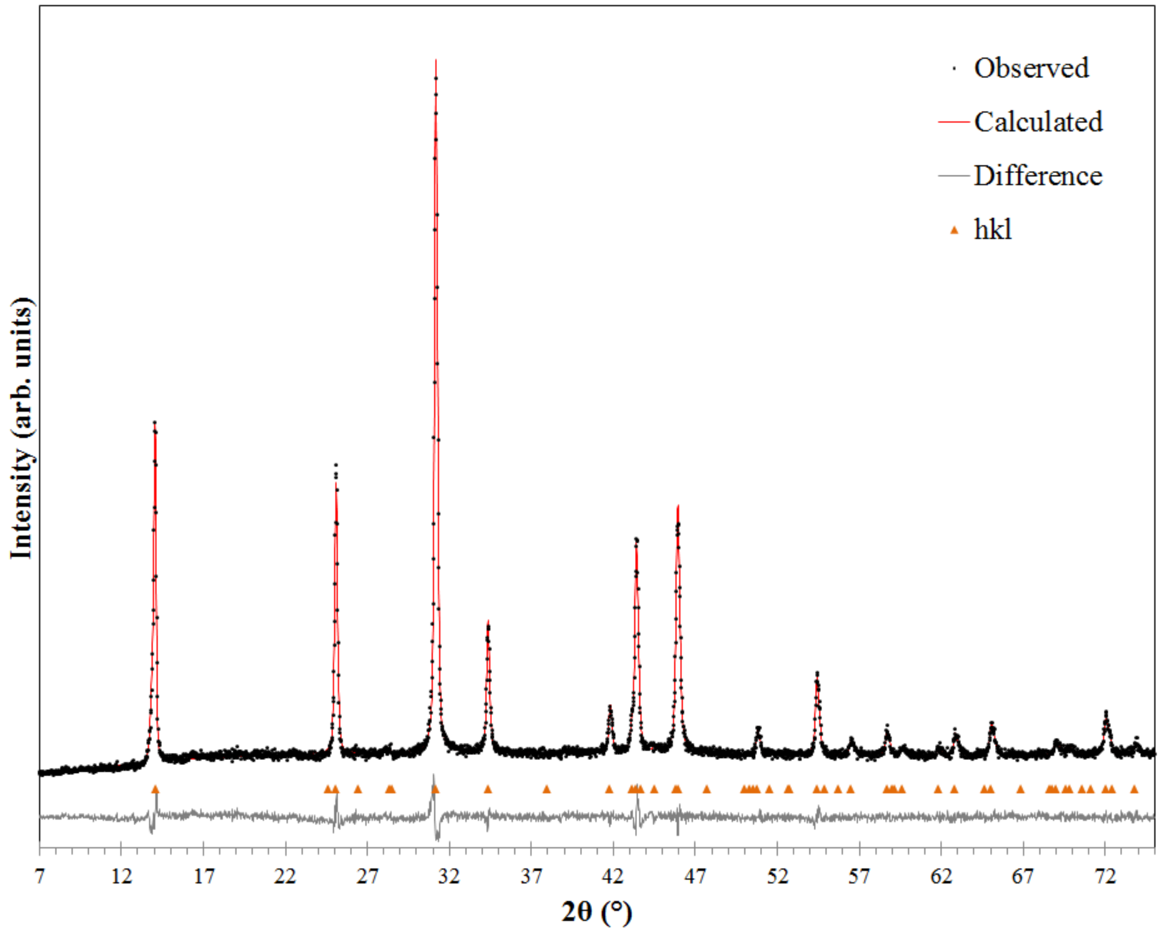


Cell Parameters	Å
a	11.2712
b	11.2712
c	11.2712

Site	Wyckoff site	x	y	z	Beq
Ag_1	4a	0.0000	0.0000	0.0000	1.7651
Bi_1	4b	½	0.0000	0.0000	1.0901
Cs	8c	¼	¼	¼	3.4308
Br	242	0.2503	0.0000	0.0000	3.6568

⬛ Successful synthesis

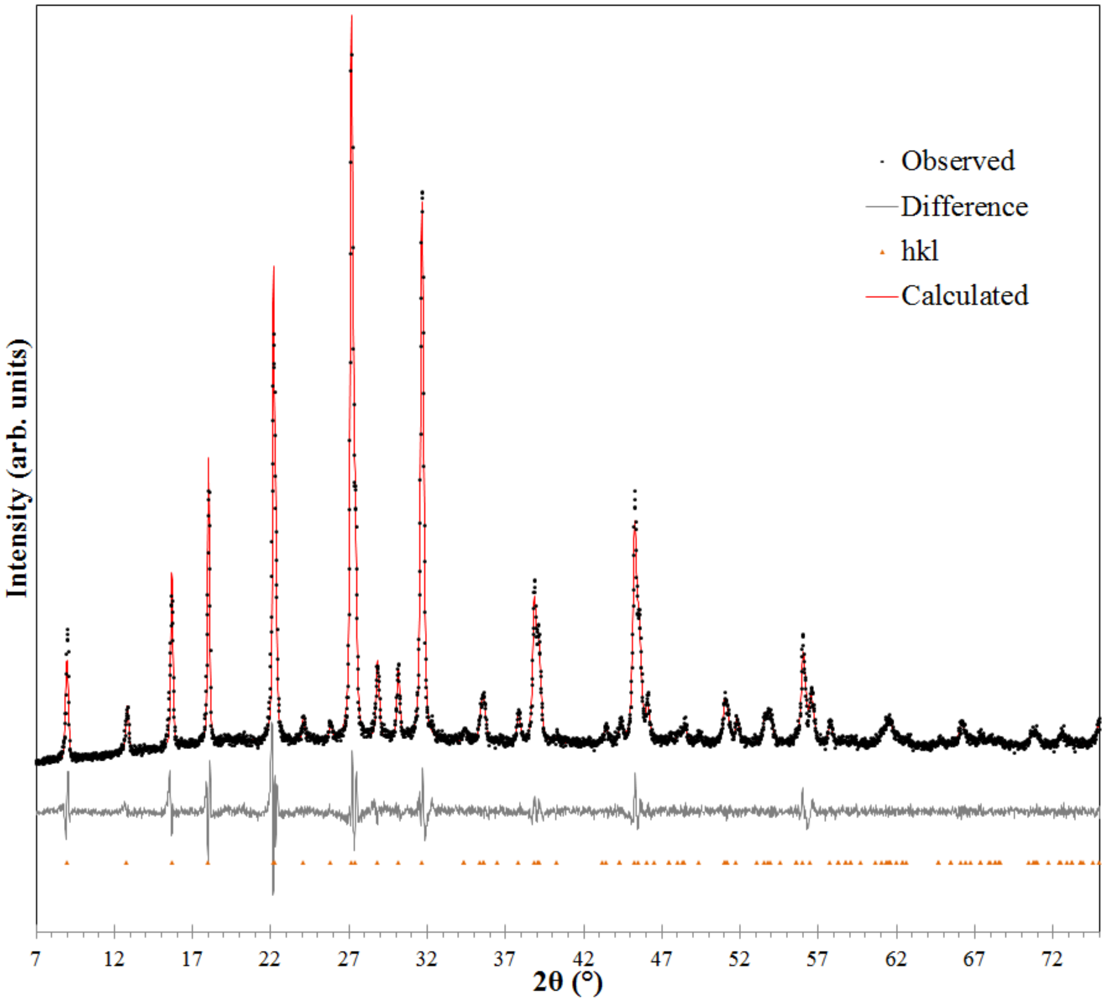
[8,10]$AgBiBr_4$	hexagonal	24.72



Cell Parameters	Å
a	12.1533
b	12.1533
c	11.1533

Successful synthesis using Pawley refinement in process of solving for sites

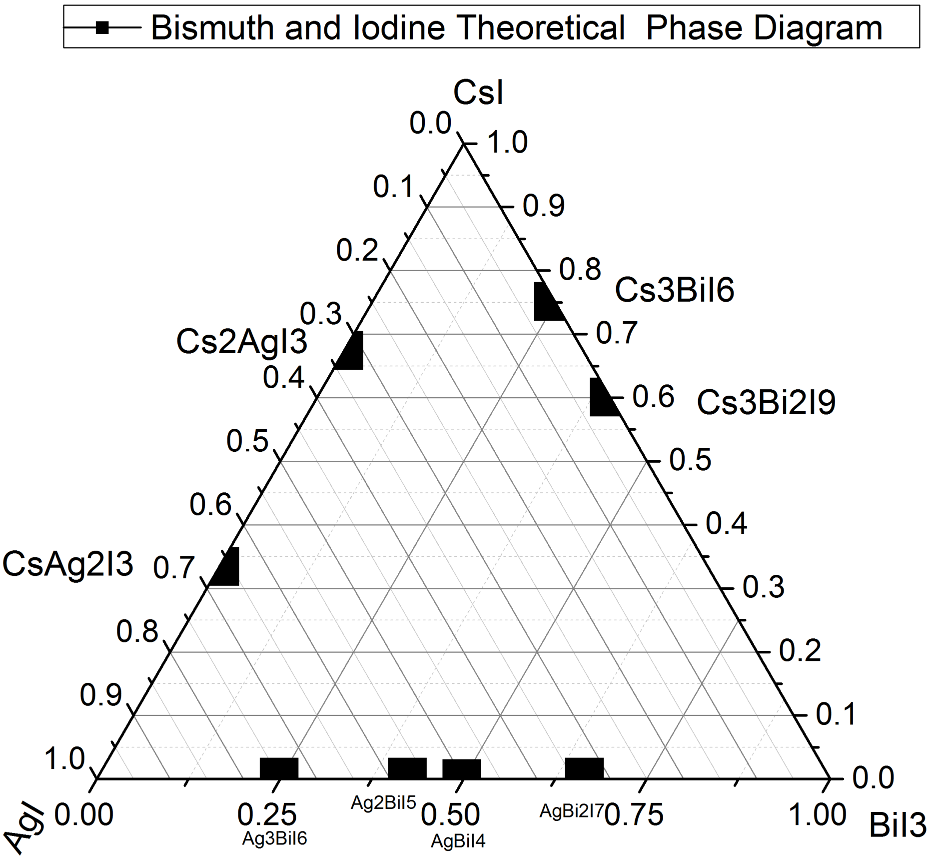
[8]Cs_3BiBr_6	hexagonal	8.093

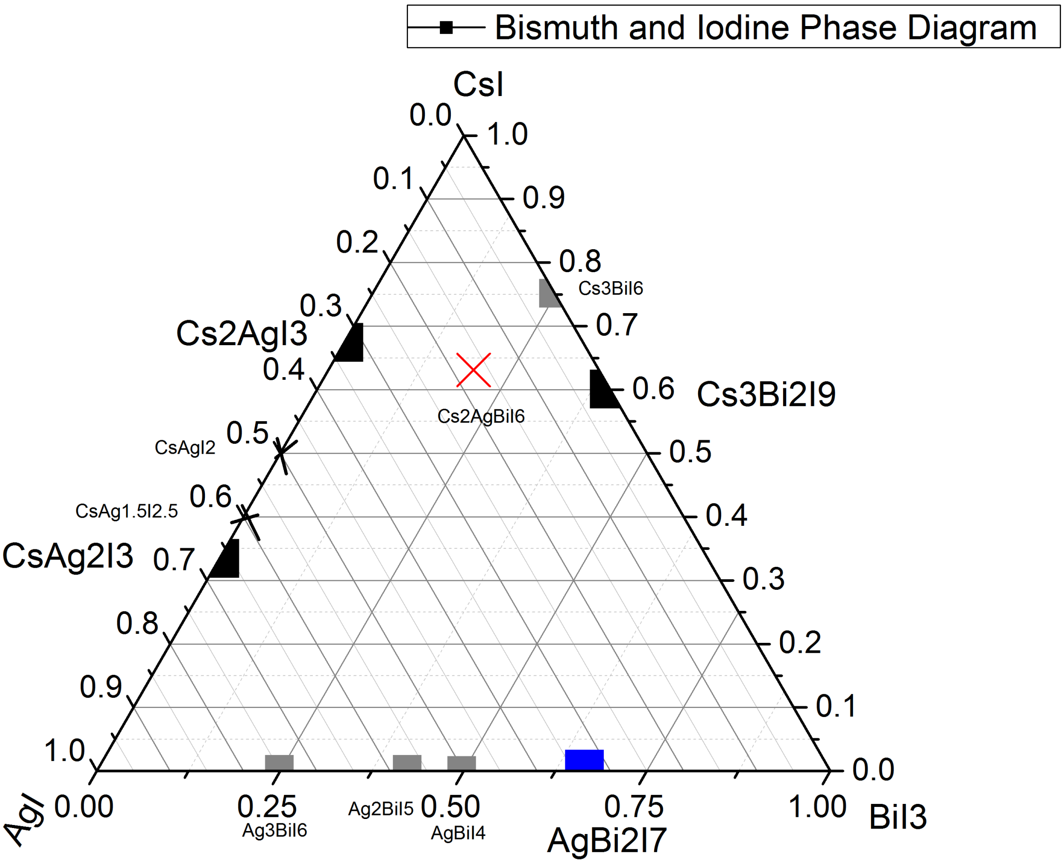


Cell Parameters	Å
a	7.9598
b	7.9598
c	9.8398

🟦 Successful synthesis using Pawley refinement in process of solving for sites

Iodine-Bismuth Results





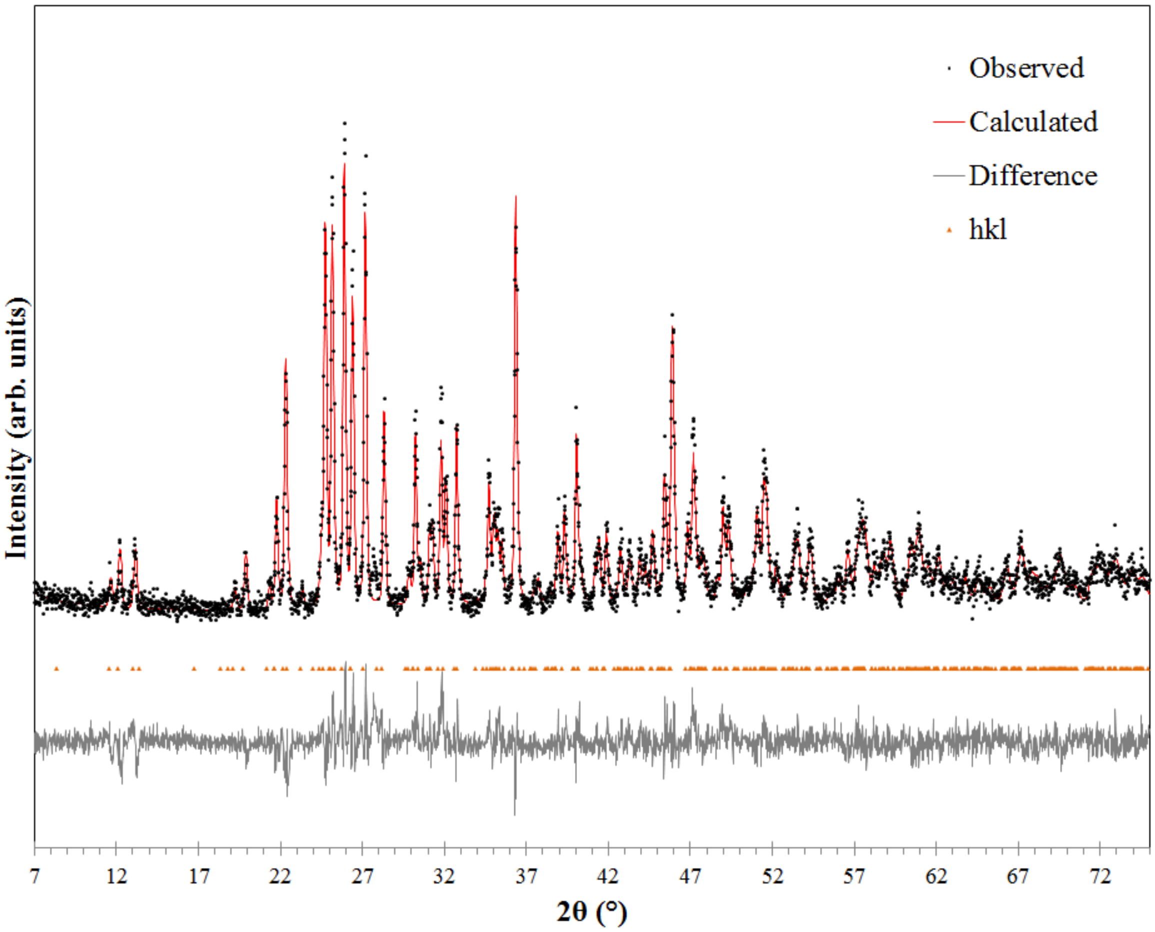
Difference Summary of Theoretical to Experimental Diagram

1. All the gray squares indicated that the products are probably not at thermodynamic equilibrium and would need to be re-heated. See XRDs below to see the mixture of products in each gray square synthesis.
2. $AgBi_2I_7$ is a black compound with no reported crystal structure but XRD shows pure compound
3. $CsAgI_2$ may contain a metastable intermediate seen when product is heated for less than 18 hours. Product changes color upon the addition of water into bright sunset orange hue, XRD of metastable and XRD of prolonged heated $CsAgI_2$ that has a mixture of Cs_2AgI_3 and $CsAg_2I_3$ contain many peak differences.
4. Different synthesis attempts were made for Cs_2AgBiI_6, all XRDs produced the same looking product regardless of the synthesis technique. XRD can tell a cohesive tell of what the product made is. When heated the unknown red product made to 350°C product turns white gray and XRD shows Cs_2AgI_3.

XRD Results of Iodine-Bismuth Results

Product	Space group	Rwp

[6]Cs_2AgI_3	Pnma #62	15.75

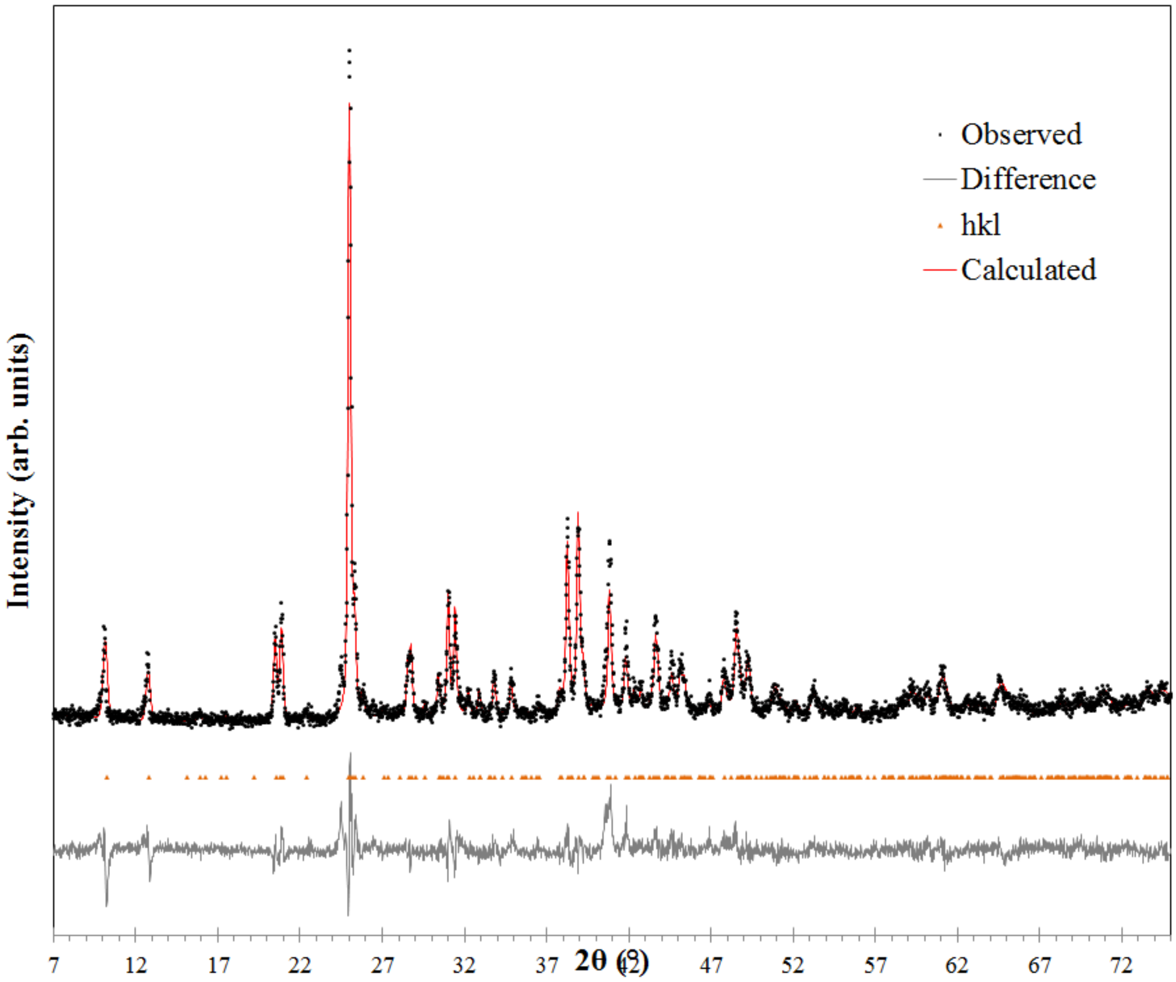


Cell Parameters	Å
a	14.5933
b	4.9533
c	15.3026

Site	Wyckoff site	x	y	z	Beq
Ag_1	4c	0.2550	¼	0.3055	-1.0956
Cs_1	4c	0.1740	¼	0.0204	-1.0956
Cs_2	4c	0.0141	¼	0.6767	-0.3664
I_1	4c	0.1319	¼	0.4522	-0.8702
I_2	4c	0.4427	¼	0.3634	-0.8702
I_3	4c	0.2759	¼	0.7131	-0.8702

■ Successful synthesis

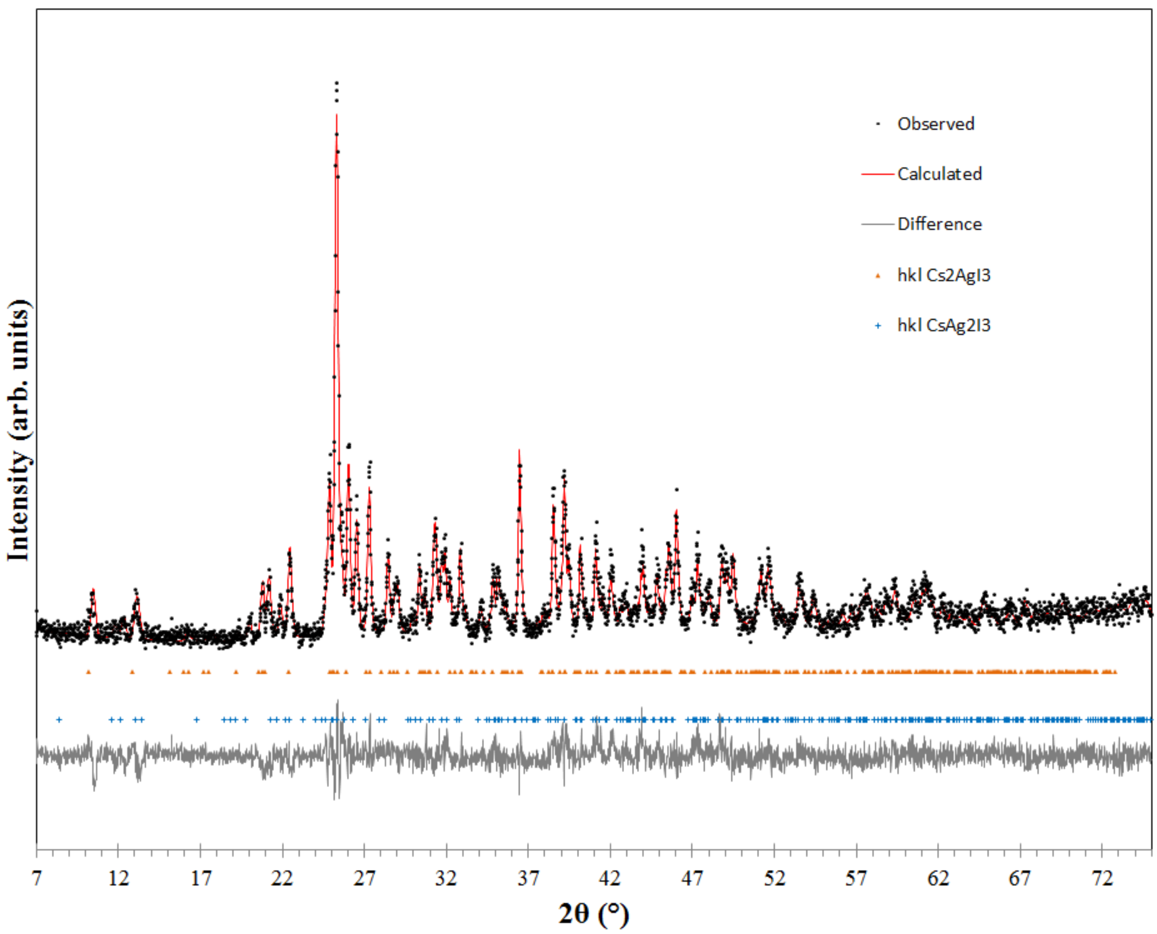
[6]$CsAg_2I_3$	Pnma #62	18.338



Cell Parameters	Å
a	13.7411
b	6.2288
c	11.0706

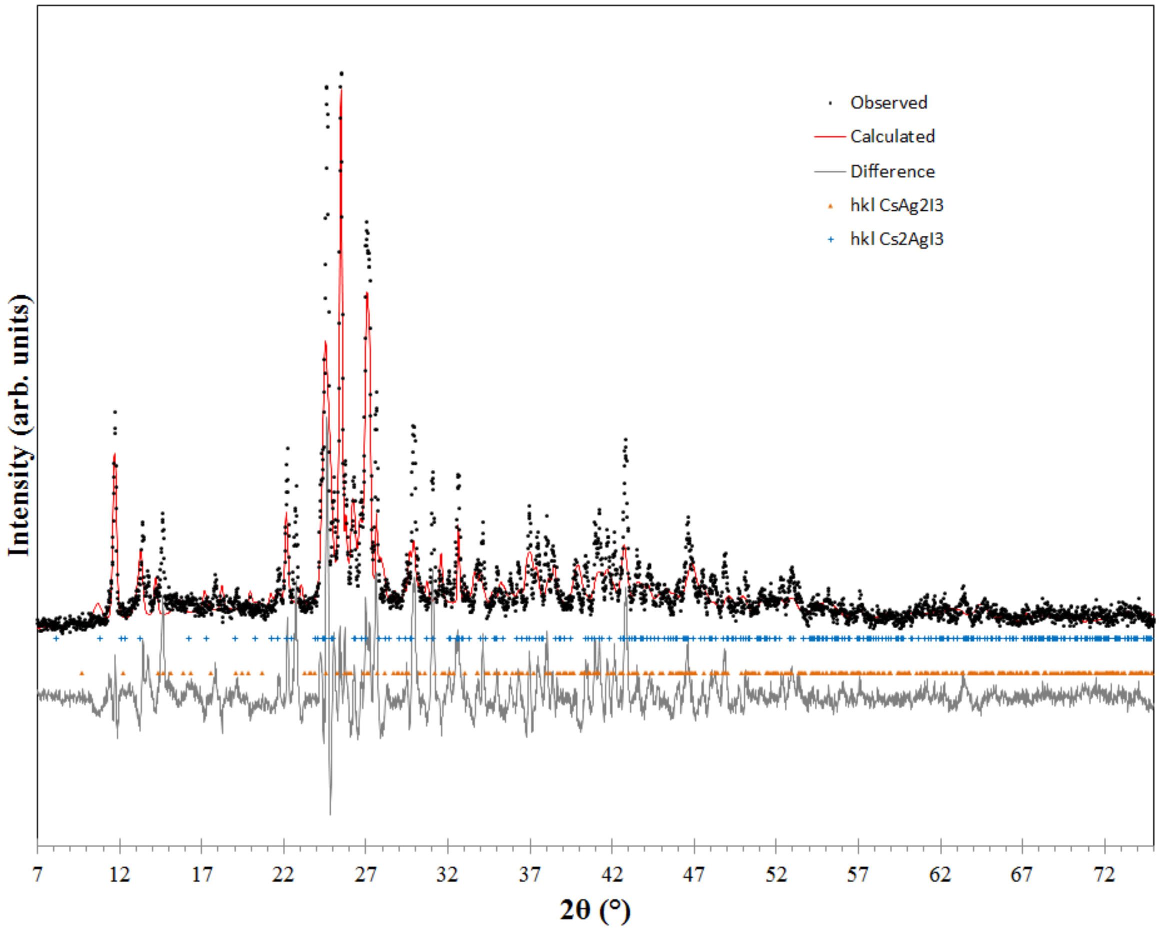
Site	Wyckoff site	x	y	z	Beq
Ag_1	8d	0.0018	0.0059	0.3339	0.6627
Cs_1	4c	0.1788	¼	0.9909	0.6627
I_1	4c	0.1270	¼	0.4942	0.0000
I_2	4c	0.3597	¼	0.2856	0.0000
I_3	4c	0.3833	¼	0.6912	0.0000

[redacted] Successful synthesis
gI2 50:50 composition of CsAg2I3 and Cs2AgI3



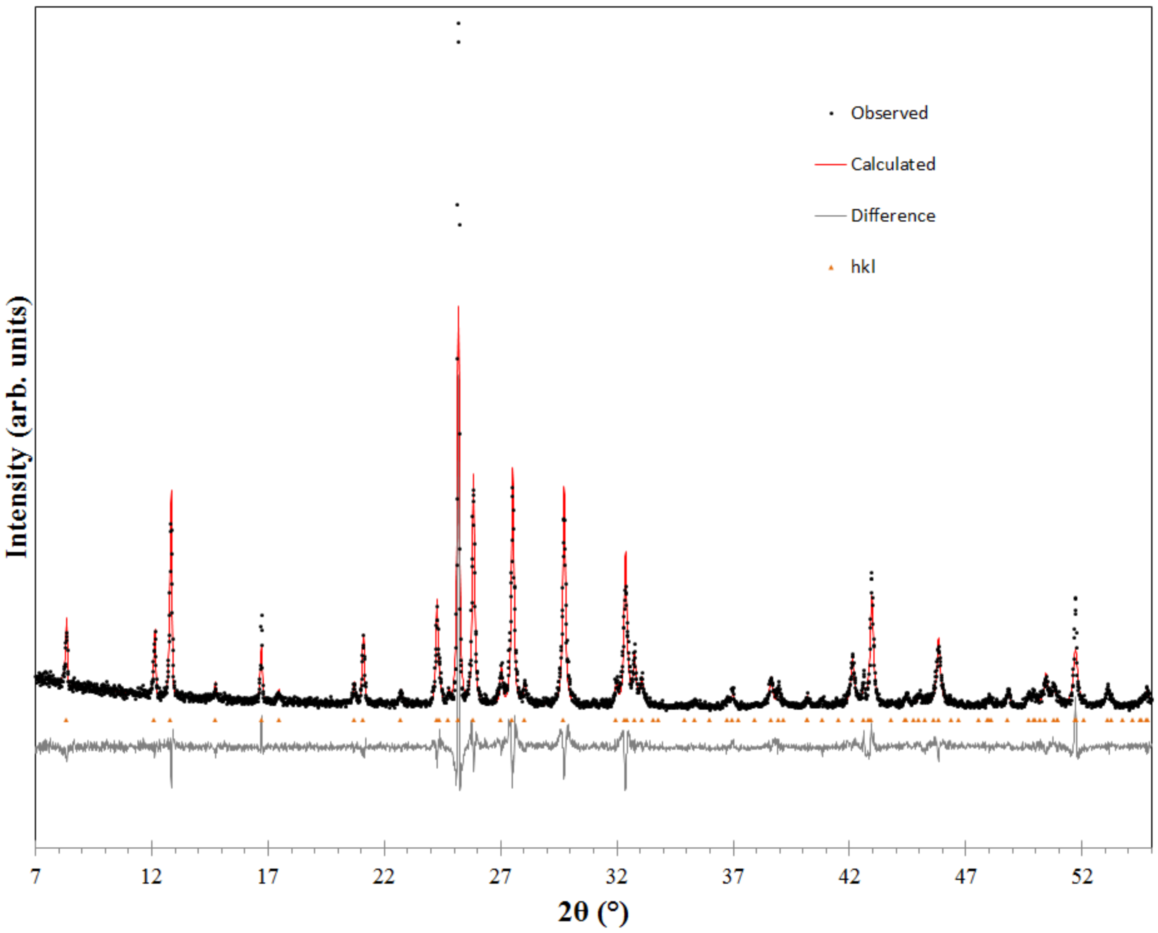
X Product is a compositional mixture of AgI and $CsAgI_2$

$CsAgI_2$ metastable



Turns bright orange upon addition of water when Cs_2AgI_3 white and $CsAg_2I_3$ sees no color change. XRD has unaccounted peaks but not clean enough to figure out crystal structure. May be an intermediate phase.

[9] $Cs_3Bi_2I_9$ (Bruker D8)	P63/mmc #194	20.43

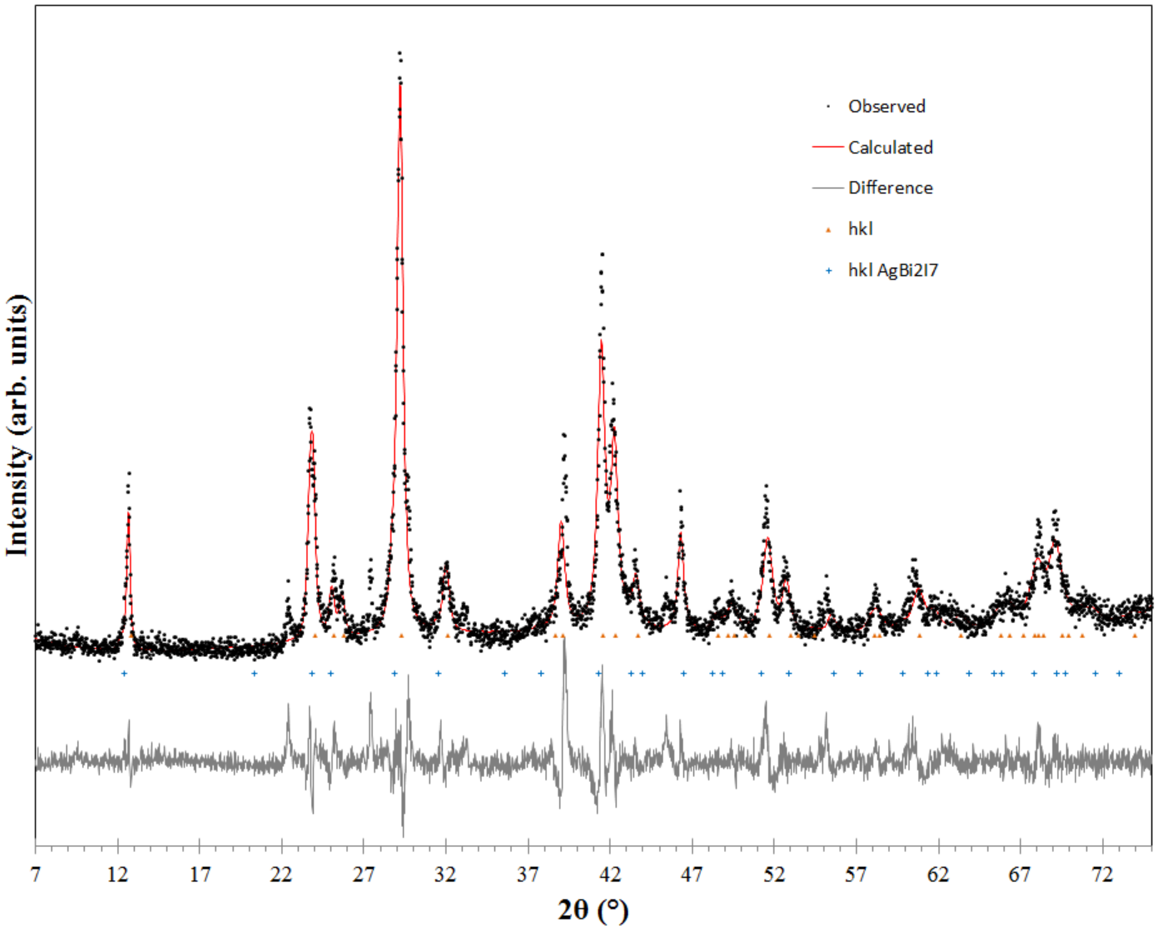


Cell Parameters	Å
a	8.4169
b	8.4169
c	21.2046

Site	Wyckoff site	x	y	z	Beq
Cs_1	2b	0.0000	0.0000	¼	3.4422
CS_2	4f	1/3	2/3	0.5824	3.4422
Bi_1	4f	1/3	2/3	0.1544	0.8086
I_1	6h	0.5080	1.0160	¼	2.3009
I_2	12k	0.1626	0.3251	0.0803	2.3009

Successful synthesis

[8,11]Ag_3BiI_6 *(includes $AgBi_2I_7$) impurity)	R3¯m #166	16.78

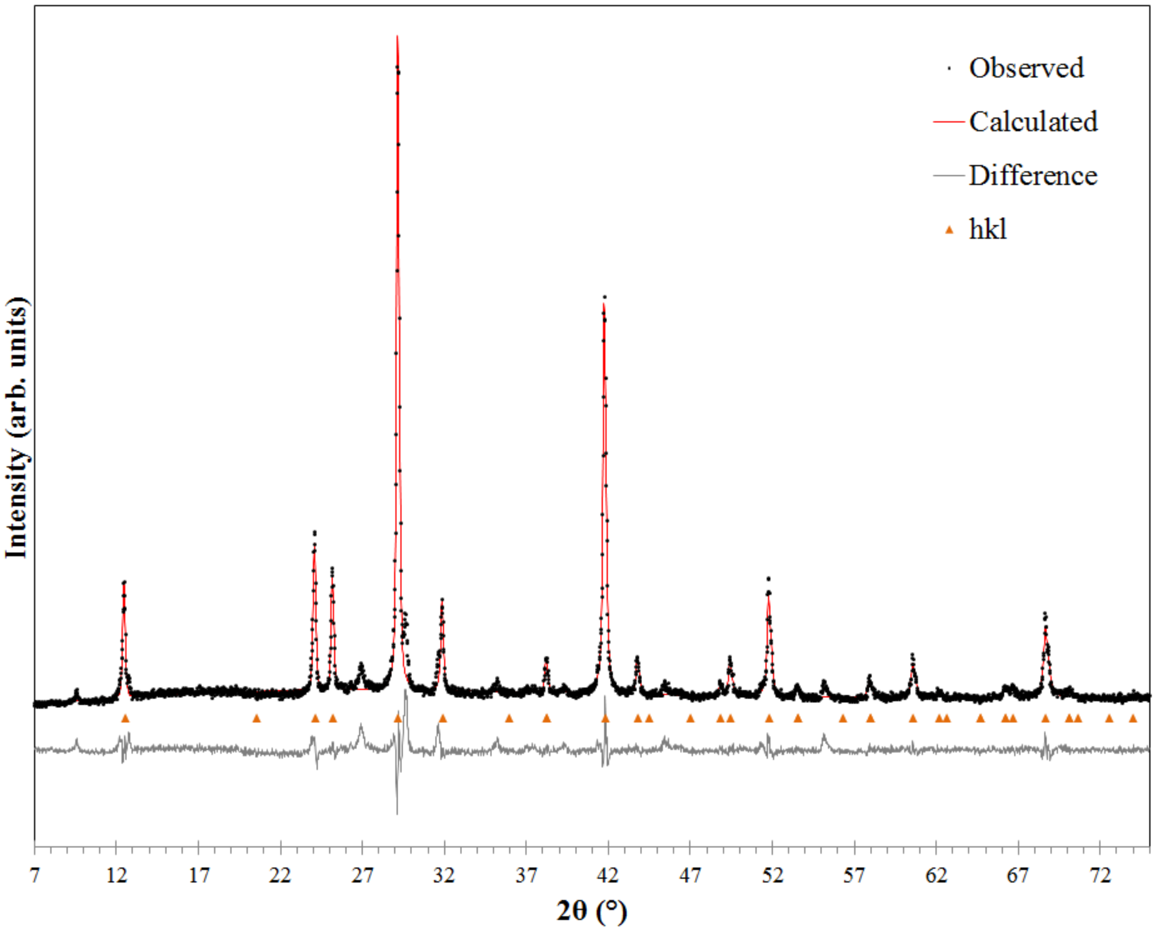


Cell Parameters	Å
a	4.3509
b	4.3509
c	20.8165

Site	Wyckoff site	x	y	z	Beq
Ag_1	3a	0.0000	0.0000	0.0000	0.1263
Ag_2	3b	0.0000	0.0000	½	20
Bi_1	3a	0.0000	0.0000	0.0000	0.8304
I_1	6c	0.0000	0.0000	0.7540	0.5585

XRD data suggests either system is not thermodynamically stable or follows that products Ag_3BiI_6 and $AgBiI_4$ only used XRD primitive measurement to identify crystal structure and could not be reproduced and the actually Ag-Bi-I system consists of Ag_2BiI_5 and $AgBi_2I_7$[11]

[11]$AgBi_2I_7$	Fd3¯¯m #227	14.167



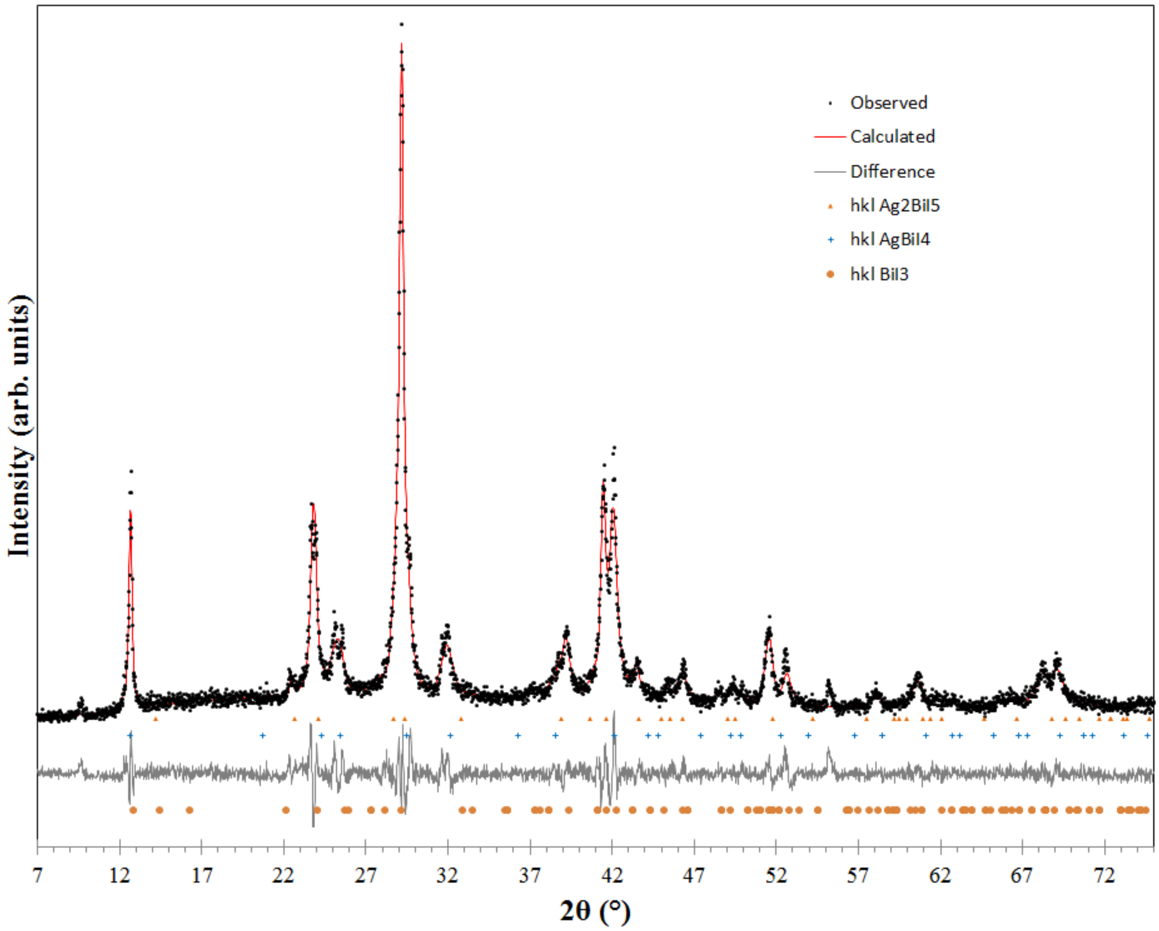
Cell Parameters	Å
a	12.3763
b	12.3763
c	12.3763

🟦 Successful synthesis using Pawley refinement in process of solving for sites

[11]Ag_2BiI_5	$R\bar{3}m$ #166	11.41

[8]$AgBiI_4$	$Fd\bar{3}m$ #227	11.41

Both XRD of $AgBiI_4$ and Ag_2BiI_5 were the same and included a mixture of each other with the same peaks in the XRD



$AgBiI_4$

Cell Parameters	Å
a	12.1201
b	12.1201
c	12.1201

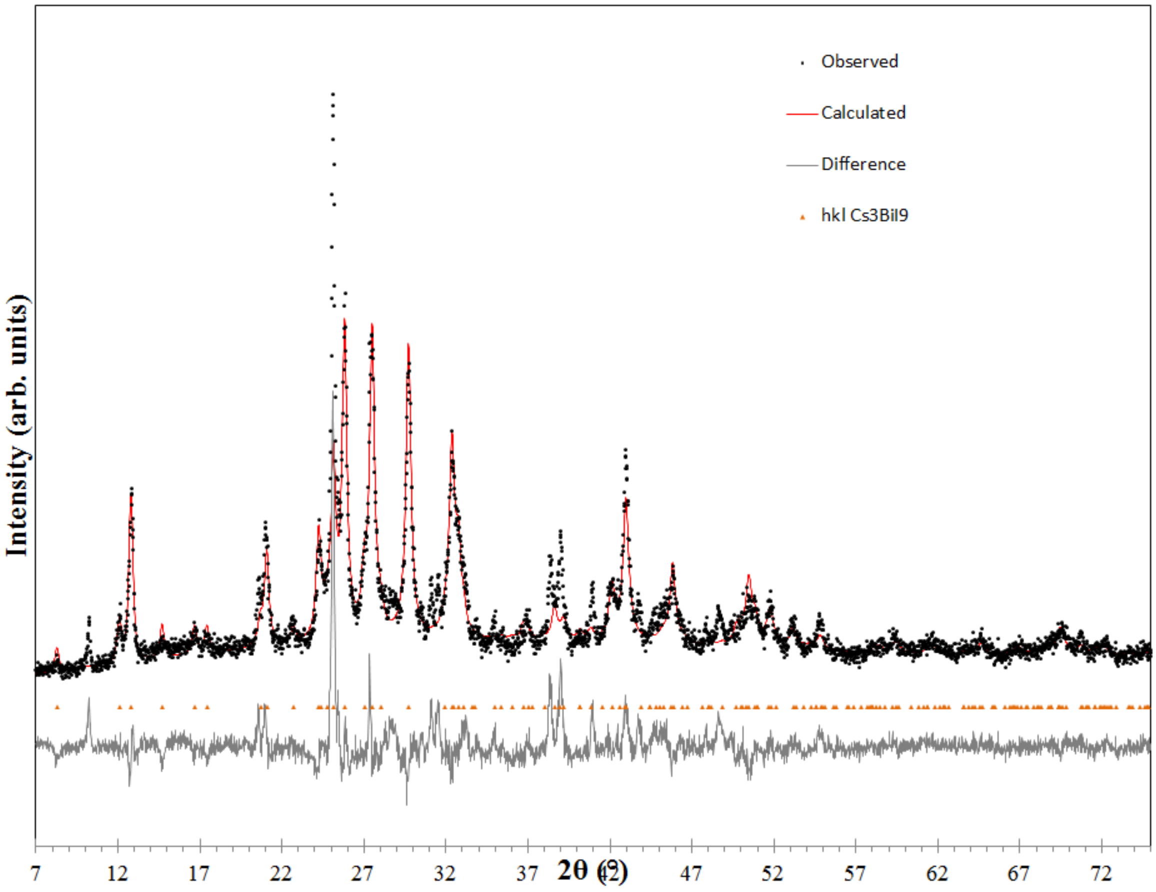
Ag_2BiI_5

Cell Parameters	Å
a	4.6223

b	4.6223
c	18.6304

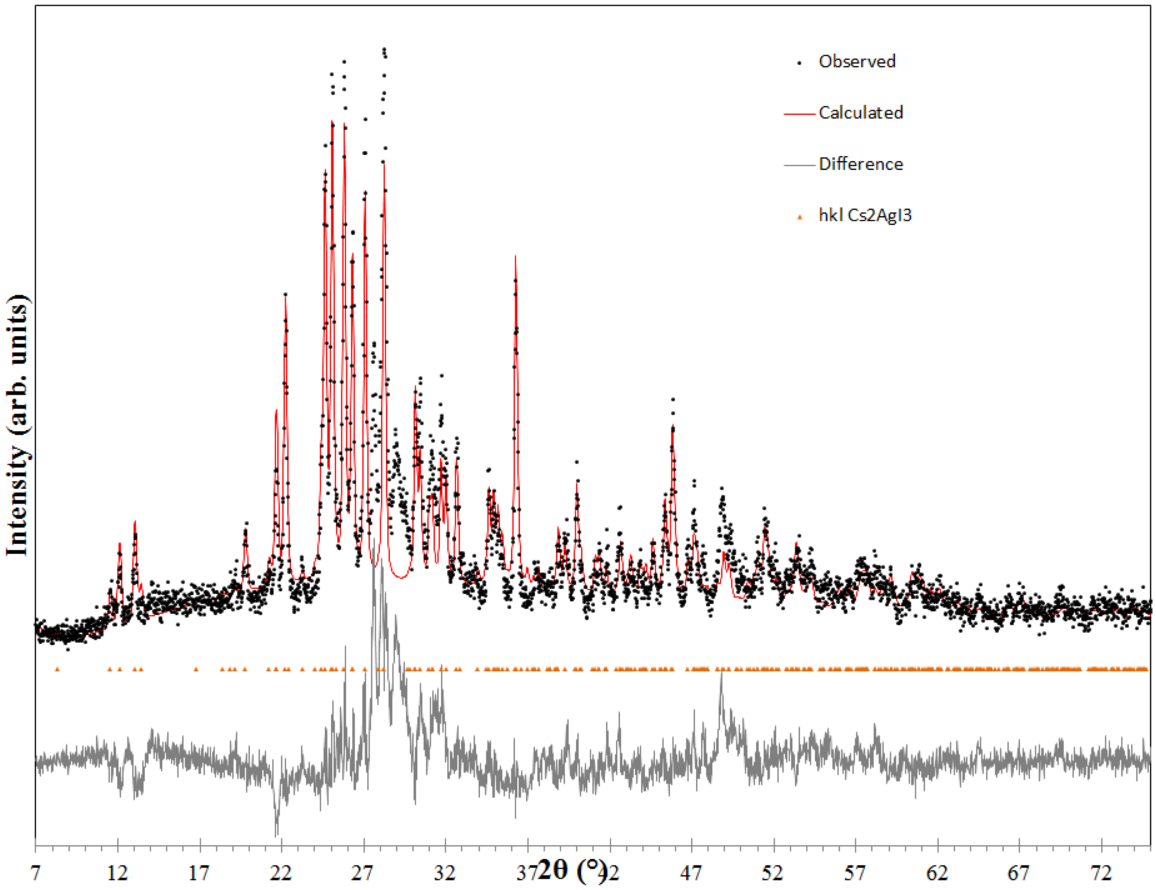
[redacted] Products have not yet reached equilibrium see Ag_3BiI_7 for more details

BiI_6 dominating $Cs_3Bi_2I_9$ product, not conclusive to declare perovskite form



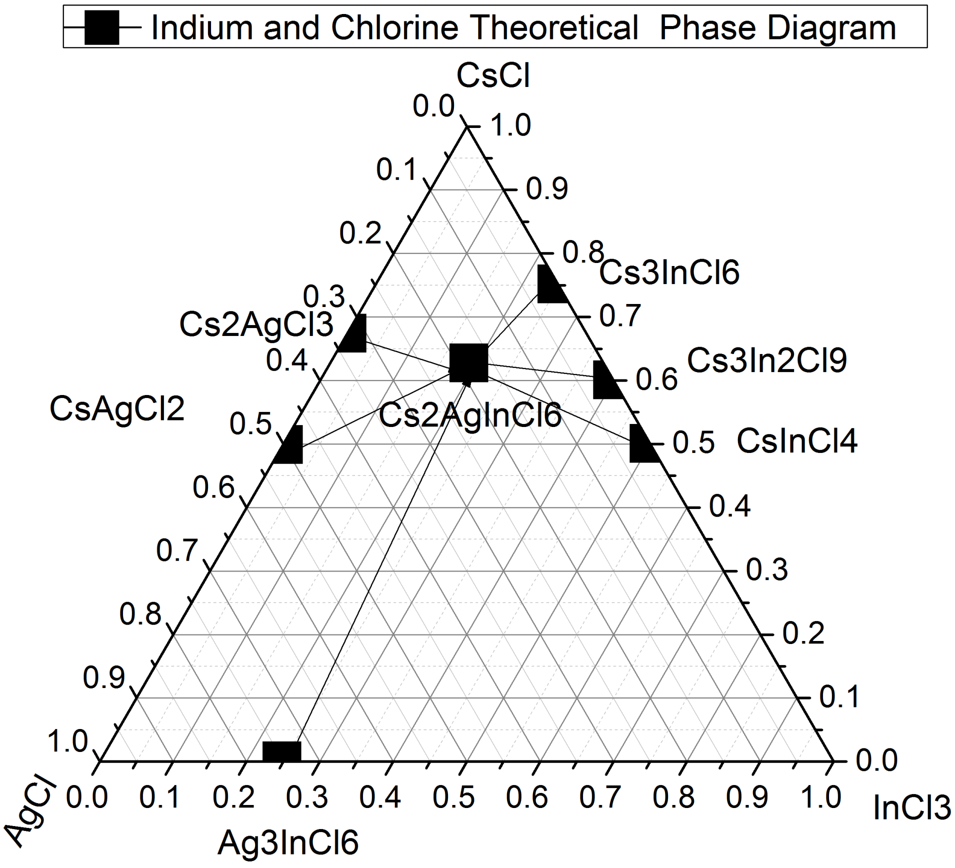
The different solvent methods and reagents combinations all yielded identical XRD patterns, the pattern is problematized by the 3-2-9 iodine having many hkl peaks as well as the Cs_2AgI_3. Adding H_3PO_2 was unsuccessful at dissolving the 3-2-9 and products made were mushy and XRDs were taken using petroleum jelly but background is too high to peak out non-3-2-9 peaks.

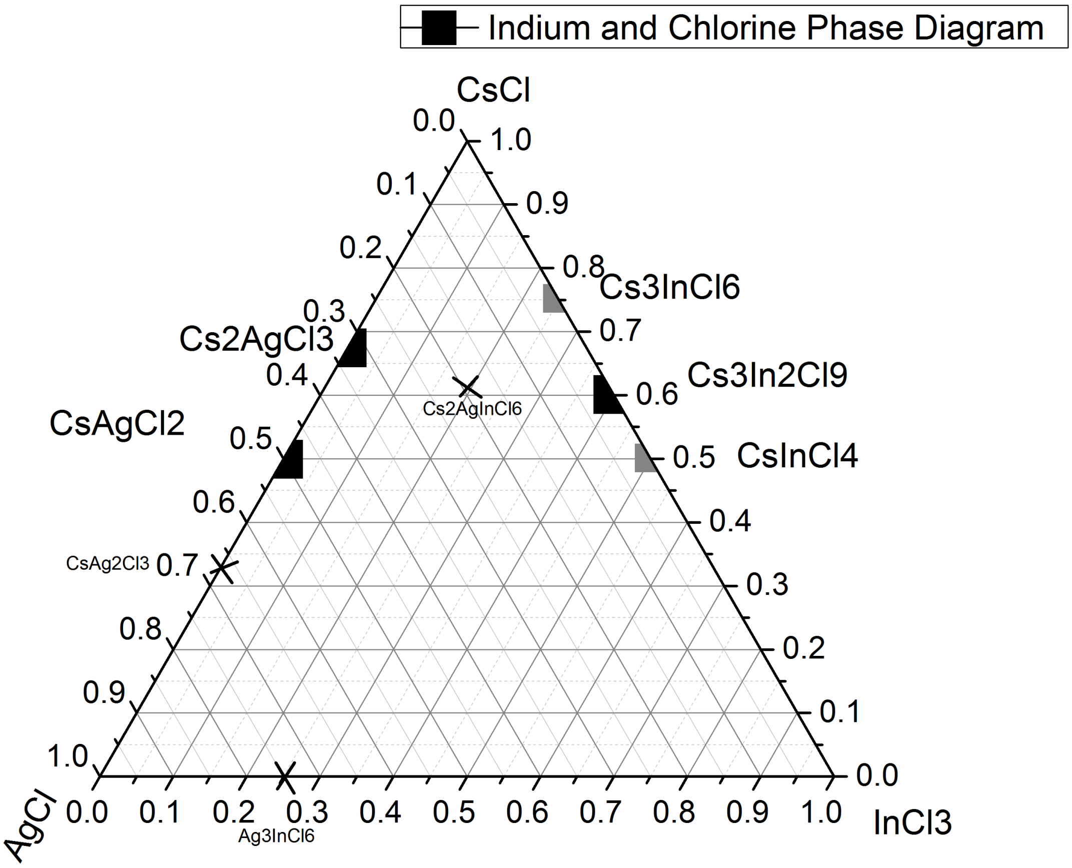
Cs_2AgBiI_6 heated at 350°C XRD shows Cs_2AgI_3 as remaining product



Indium-Chlorine Results

Phase Diagram does not represent a full theoretical list of all potential products of the diagram





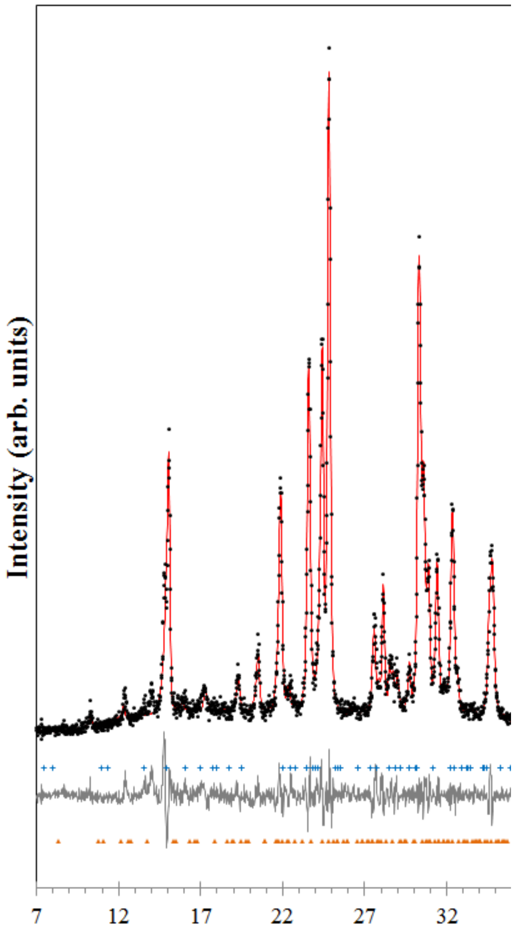
Difference Summary of Theoretical to Experimental Diagram

1. Ag_3InCl_6 is hygroscopic and not successfully synthesized
2. $CsAg_2Cl_3$ * see Cl-Bi Phase Diagram
3. $Cs_2AgInCl_6$ is hygroscopic and XRD is too noisy to confirm the double perovskite phase
4. Gray squares indicate that the Cs-In-Cl products look like a mixture of products and may not have reached equilibrium, but products are also hygroscopic

XRD Chlorine-Indium Results

Product	Space group	Rwp

[12]Cs_3InCl_6 *(includes $CsInCl_4$ impurity)	P4 #75	11.026



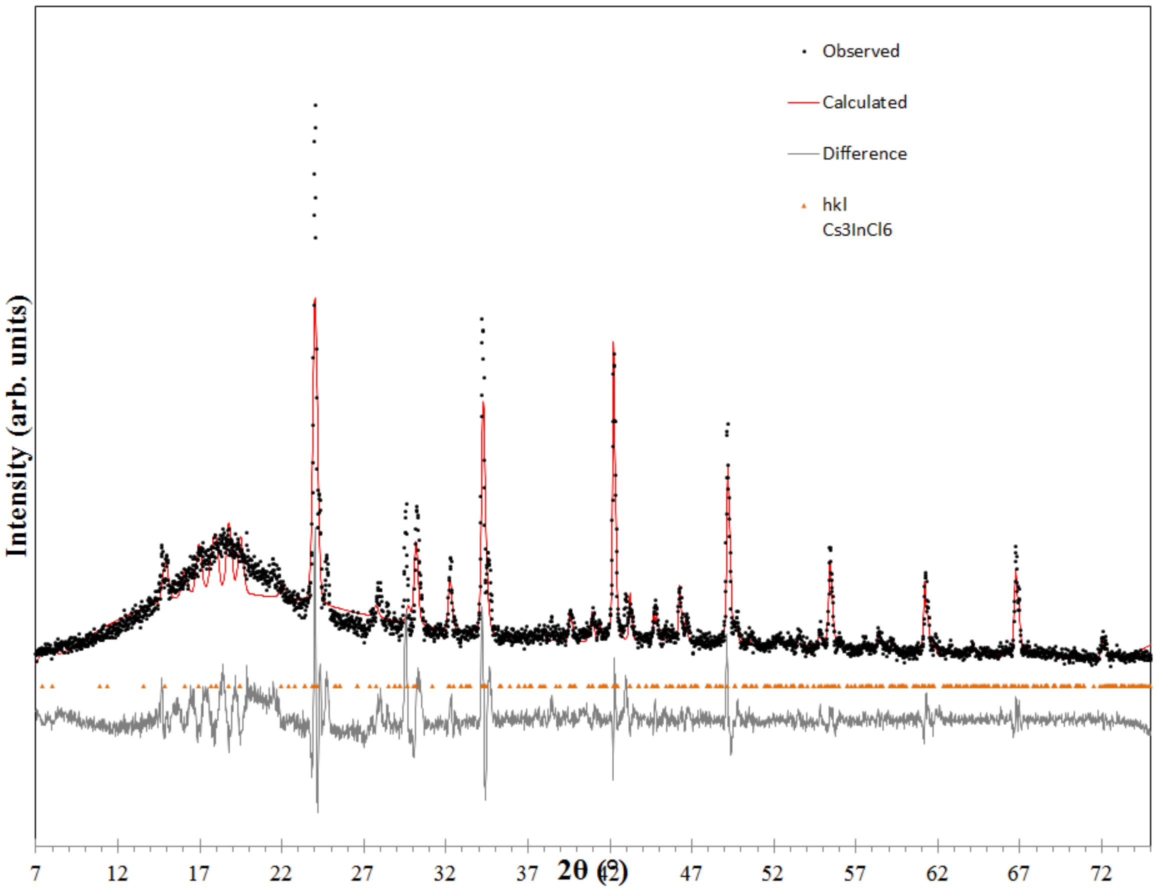
Cell Parameters	Å
a	11.0786
b	11.0786
c	11.9236

$CsInCl_4$	Pmcn #62	11.026

Cell Parameters	Å
a	11.0360
b	11.0360
c	11.0360

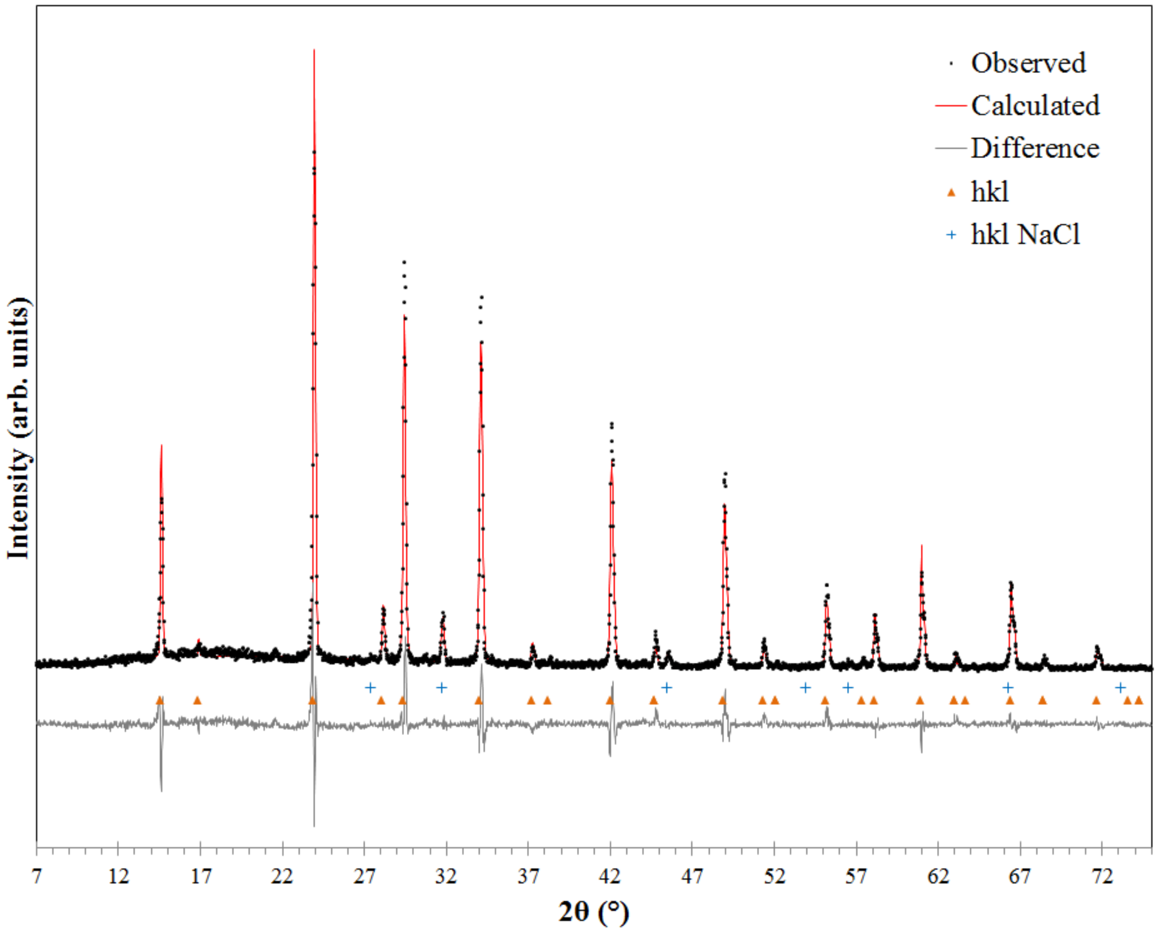
System is not thermodynamically stable yet, and products are very hygroscopic synthesis methods need to include a greater nitrogen enriched environment[12]

$Cs_2AgInCl_6$ perovskite phase not definitive to declare, product is hygroscopic



X Used petroleum jelly on XRD cannot declare double perovskite phase

[13]$Cs_2NaInCl_6$ *(contains NaCl impurity)	Fm-3m #225	18.88



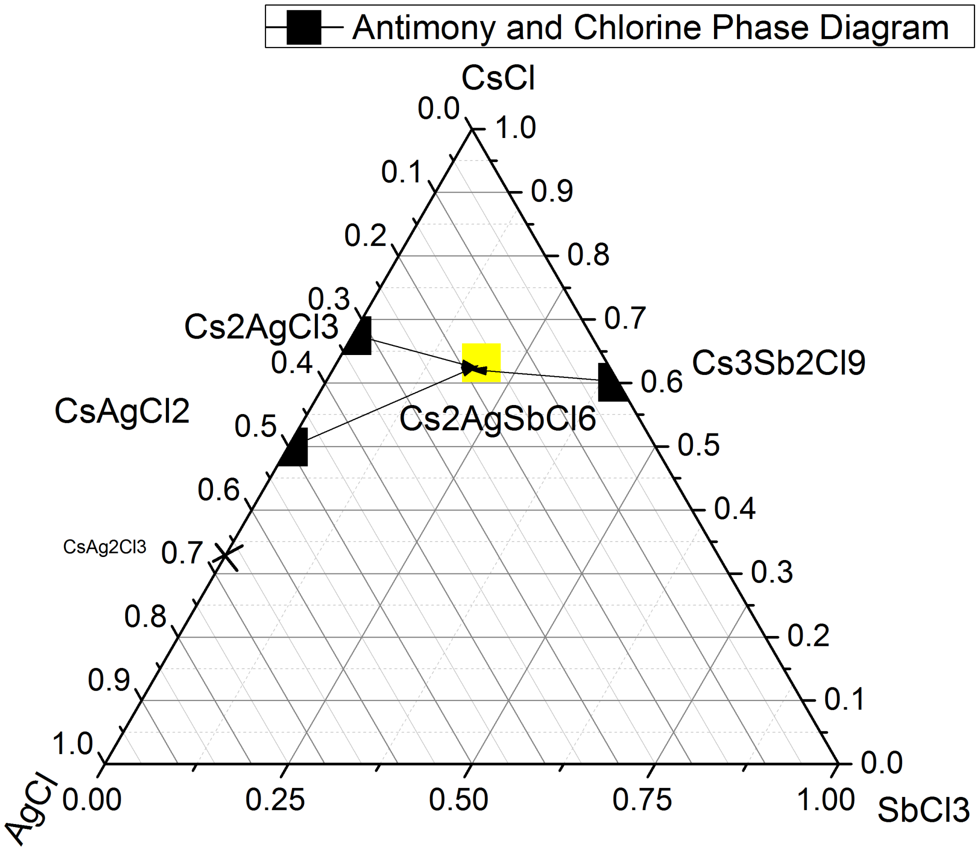
Cell Parameters	Å
a	10.5265
b	10.5265
c	10.5265

Site	Wyckoff site	x	y	z	Beq
Na_1	4a	0.0000	0.0000	0.0000	1.9700
In_1	4b	½	½	½	1.9700
Cs	8c	¼	¼	¼	2.7560
Cl	24e	0.2518	0.0000	0.0000	2.4643

[redacted]

synthesis

Chlorine- Antimony Results



Future work needs to be done to complete both the potential products listed on the axis of In-Cl and Sb-Cl phase diagram. H_3PO_2 also dissolves the 3-2-9 product and therefore theoretical would aid in the purity of synthesis of the double perovskite phase.

Summary of Products synthesized

Product Goal	Method of Synthesis	concentration soultion (M)	Temperture/Time (oC/hr)	Successful	Product Made	Color
Cs3Bi2Cl9	solution	12.1 HCl	100 solution	yes	Cs3BiCl9	white
[14]AgBiCl4	solution	12.1 HCl	100 solution	hygroscopic	n/a	silver
Cs2AgBiCl6	solution	12.1 HCl	100 solution	yes	Cs2AgBiCl6	yellow
CsAgCl2	solid grinding	n/a	400 */ 72hr	yes	CsAgCl2	white
Cs2AgCl3	solid grinding	n/a	200/ 72hr	yes	Cs2AgCl3	white
CsAg2Cl3	solid grinding	n/a	200/ 72hr	no	CsAgCl2 and AgCl	white/purple
CsAgBr2	solid grinding	n/a	200/ 72hr	yes	CsAgBr2	white/yellow
Cs2AgBr3	solid grinding	n/a	200/ 72hr	yes	Cs2AgBr3	white
CsAg2Br3	solid grinding	n/a	200/ 72hr	no	CsAgBr2 and AgBr	white/yellow
CsAgI2 *	solid grinding	n/a	200/ 72hr	maybe	CsAgI2 (2-1,1-2)	light orange
Cs2AgI3	solid grinding	n/a	200/ 72hr	yes	Cs2AgI3	white
CsAg2I3	solid grinding	n/a	200/ 72hr	yes	CsAg2I3	orange
CsAg1.5I2.5	solid grinding	n/a	200/ 18hr	no	CsAg2I3 and AgI	orange
Cs3BiCl6**	solid grinding	n/a	200/ 72hr	some	Cs3BiCl6 Cs3Bi2Cl9	white
Cs3InCl4	solution	5mL 12.1 and 5mL 6	150 solution	some	Cs3InCl4 CsInCl4	white
CsInCl4	solution	5mL 12.1 and 5mL 6	150 solution	hygroscopic	yes	white
Ag3InCl6	solution	5mL 12.1 and 5mL 6	150 solution	hygroscopic	n/a	white
Cs2AgInCl6	solution	5mL 12.1 and 5mL 6	150 sol and 200/ 18hr	hygroscopic	n/a	white/purple
Cs2NaInCl6	solurion	5mL 12.1 and 5mL 6	18 hr	yes	Cs2NaInCl6	white
AgBiBr4	solution	HBr	150 solution	yes	AgBiBr4	curry yellow
Cs3BiBr6	solution	HBr	150 solution	some	Cs3BiBr6 mostly Cs3Bi2Br9?	bright yellow
Cs3BiI6	solid grinding	n/a	150/ 72 hr	no	Cs3Bi2I9	bright red
AgBiI4**	solid grinding BiI3	n/a	150/ 72 hr	some	mixture AgBiI4 Ag2BiI5	black
Ag2BiI5**	solid grinding BiI3	n/a	150/ 72 hr	some	mixture AgBiI4 ? Ag2BiI6 ?	black
AgBi2I7	solid grinding BiI3	n/a	150/ 72 hr	yes	AgBi2I7	black
Ag3BiI6**	solid grinding BiI3	n/a	150/ 72 hr	yes	Ag3BiI6 ?	black
Cs2AgBiI6’	sg (2-1)	n/a	150/ 72 hr	maybe	Cs2AgI3 Cs3Bi2I9 ?	dark red
Cs2AgBiI6’	sg (1-2) and CsI	n/a	150/ 72 hr	maybe	Cs2AgI3 Cs3BiI9 ?	dark red
Cs2AgBiI6’	solvent methanol	n/a	150/ 72 hr	maybe	Cs2AgI3 Cs3Bi2I9 ?	red
Cs2AgBiI6’	solvent ethanol	n/a	150/ 72 hr	maybe	Cs2AgI3 Cs3Bi2I9 ?	red
Cs2AgBiI	solvent acetonitrile	n/a	350/ 72 hr	maybe	Cs2AgI3 and Cs3Bi2I9	red
Cs2AgBiI6	solvent etoh and H3PO4	n/a	n/a	liquid	n/a	red

*May include a metastable product, but at thermodynamic equilibrium $CsAgI_2$ does not exsit