Supporting Information for

The synthesis and structure-property relation analysis of metal chalcohalide crystals $Cs_2InPS_4X_2$ (X = Cl, Br) with mixed anions

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1. **Table S1**
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1. **Table S1** Atomic coordinates, equivalent isotropic displacement parameters and bond valence sums (BVS) for $Cs_2InPS_4Cl_2$.

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq} (Å^2) [a]	BVS
In	4e	0.6883(3)	0.49799(3)	0.44549(2)	0.022(8)	3.13
P	4e	0.63516(10)	0.4093(13)	0.63873(6)	0.0205(2)	5.28
S1	4e	0.53706(10)	0.27084(13)	0.54177(6)	0.025(2)	–1.93
S2	4e	0.72487(12)	0.27517(14)	0.73178(6)	0.0305(2)	–2.17
S3	4e	0.78773(11)	0.54875(15)	0.58805(6)	0.0302(2)	–2.21
S4	4e	0.4779(11)	0.56143(15)	0.6774(6)	0.0303(2)	–2.16
Cs1	4e	0.86102(3)	0.00384(4)	0.58954(2)	0.03719(9)	1.05
Cs2	4e	1.0758(3)	0.50693(4)	0.77278(2)	0.03799(9)	0.97
Cl1	4e	0.83828(11)	0.256(14)	0.40326(7)	0.0337(2)	–0.97
Cl2	4e	0.82882(11)	0.73668(14)	0.39243(7)	0.0341(2)	–0.98

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

2. Table S2 Atomic coordinates, equivalent isotropic displacement parameters and bond valence sums (BVS) for $Cs_2InPS_4Br_2$.

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq} (Å^2) [a]	BVS
In	4e	0.68268(2)	0.5001(3)	0.44506(2)	0.02251(6)	3.35
P	4e	0.36414(8)	0.41032(10)	0.36164(5)	0.02022(16)	5.27
S1	4e	0.46158(9)	0.27594(10)	0.45899(5)	0.02546(18)	–1.90
S2	4e	0.27319(9)	0.2773(10)	0.26947(5)	0.02834(18)	–2.17
S3	4e	0.51639(9)	0.55702(12)	0.32225(5)	0.0301(2)	–2.14
S4	4e	0.21811(9)	0.55034(12)	0.41183(5)	0.03012(19)	–2.18
Cs1	4e	0.55931(3)	0.00119(3)	0.2732(2)	0.03741(7)	1.03
Cs2	4e	0.35176(3)	0.49998(3)	0.0912(2)	0.03712(7)	1.07
Br1	4e	0.82737(4)	0.25308(4)	0.39072(2)	0.03299(9)	–1.17
Br2	4e	0.83779(4)	0.74712(4)	0.40035(2)	0.03308(9)	–1.16

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3. Table S3 Selected band distances (Å) and band angles (°) for $Cs_2InPS_4Cl_2$.

In–S1	2.8668(11)	Cs1–S4^4	4.0030(11)
In–S1^2	2.8374(10)	Cs1–Cl1	3.6257(11)
In–S3	2.4675(10)	Cs1–Cl1^3	3.5144(11)
In–S4^2	2.4819(10)	Cs1–Cl2^1	3.5822(11)
In–Cl1	2.5129(11)	Cs1–Cl2^5	3.8365(12)
In–Cl2	2.5063(11)	Cs2–S1^6	3.9216(11)
P1–S1	2.0680(14)	Cs2–S2^6	3.5548(12)
P1–S2	1.9741(14)	Cs2–S2	3.8154(12)
P1–S3	2.0658(15)	Cs2–S3	3.8986(11)
P1–S4	2.0691(14)	Cs2–S4^4	3.6177(12)
Cs1–S1	3.7524(10)	Cs2–Cl1^7	3.7422(12)
Cs1–S2	3.5039(11)	Cs2–Cl1^1	3.6001(12)
Cs1–S2^4	3.6031(11)	Cs2–Cl2^1	3.5118(12)
Cs1–S3^5	3.6166(12)	Cs2–Cl2^8	3.5705(12)
S1—In—Cs2^1	140.42(2)	S2—P—S4	109.76(6)
S1^2—In—Cs2^1	121.41(2)	S2—P—S3	108.77(6)
S1^2—In—S1	85.37(3)	S4—P—Cs1	161.98(5)
Cl1—In—Cs2^1	54.25(3)	S4—P—Cs2^4	85.85(5)
Cl1—In—S1	91.44(3)	S3—P—Cs1	85.01(5)
Cl1—In—S1^2	163.52(3)	S3—P—Cs2^4	161.07(5)
Cl2—In—Cs2^1	52.22(3)	S3—P—S1	104.36(6)
Cl^2—In—S1^2	89.69(3)	S3—P—S4	113.01(7)
Cl^2—In—S1	166.31(3)	In—Cl1—Cs1	99.19(3)
Cl2—In—Cl1	96.77(4)	In—Cl1—Cs1^3	156.07(4)
S4^2—In—Cs2^1	71.23(3)	In—Cl1—Cs2^1	91.25(3)
S4^2—In—S1^2	75.50(3)	In—Cl1—Cs2^9	101.53(3)
S4^2—In—S1	90.88(3)	Cs1^3—Cl1—Cs1	71.46(2)
S4^2—In—Cl1	88.41(4)	Cs1—Cl1—Cs2^9	99.47(3)

S4^{2}—In—Cl2	100.25(4)	Cs1^{3}—Cl1—Cs2^{9}	101.74(3)
S3—In—Cs2^{1}	126.19(3)	Cs1^{3}—Cl1—Cs2^{1}	93.88(3)
S3—In—S1	75.08(3)	Cs2^{1}—Cl1—Cs1	163.39(3)
S3—In—S1^{2}	92.85(4)	Cs2^{1}—Cl1—Cs2^{9}	90.98(2)
S3—In—Cl1	101.96(4)	In—Cl2—Cs1^{10}	96.22(3)
S3—In—Cl2	92.46(4)	In—Cl—Cs1^{1}	149.52(4)
S3—In—S4^{2}	162.58(4)	In—Cl2—Cs2^{11}	104.40(3)
Cs1—P—Cs2^{4}	76.160(19)	In—Cl2—Cs2^{1}	93.44(3)
S1—P—Cs1	68.92(4)	Cs1^{1}—Cl2—Cs1^{10}	68.31(2)
S1—P—Cs2^{4}	70.79(4)	Cs2^{11}—Cl2—Cs1^{10}	98.70(3)
S1—P—S4	104.40(6)	Cs2^{11}—Cl2—Cs1^{1}	103.85(3)
S2—P—Cs1	62.11(4)	Cs2^{1}—Cl2—Cs1^{10}	160.38(3)
S2—P—Cs2^{4}	60.57(4)	Cs2^{1}—Cl2—Cs1^{1}	95.10(3)
S2—P—S1	116.53(6)	Cs2^{1}—Cl2—Cs2^{11}	95.37(3)

Symmetry codes: (1)2-*X*,1-*Y*,1-*Z*; (2)1-*X*,1-*Y*,1-*Z*; (3)2-*X*, -*Y*,1-*Z*; (4)3/2-*X*,-1/2+*Y*,3/2-Z; (5)+*X*,-1+*Y*,+*Z*; (6)3/2-*X*,1/2+*Y*,3/2-*Z*; (7)1/2+*X*,1/2-*Y*,1/2+*Z*; (8)1/2+*X*,3/2-*Y*,1/2+*Z*; (9)-1/2+*X*,1/2-*Y*,-1/2+*Z*; (10)+*X*,1+*Y*,+*Z*; (11)-1/2+*X*,3/2-*Y*,-1/2+*Z*

4. Table S4 Selected band distances (Å) and band angles (°) for $Cs_2InPS_4Br_2$.

In–S1	2.8489(9)	Cs1–S4^{2}	3.8548(9)
In–S1^{1}	2.8752(9)	Cs1–Br1	3.6757(5)
In–S3	2.4834(8)	Cs1–Br1^{4}	3.6339(5)
In–S4^{1}	2.4723(8)	Cs1–Br2^{3}	3.8233(5)
In–Br1	2.6533(4)	Cs1–Br2^{4}	3.7111(5)
In–Br2	2.6545(4)	Cs2–S1^{5}	3.7986(9)
P1–S1	2.0664(11)	Cs2–S2^{5}	3.5193(9)
P1–S2	1.9763(11)	Cs2–S2	3.5984(9)
P1–S3	2.0680(12)	Cs2–S3	3.9767(9)
P1–S4	2.0712(12)	Cs2–S4^{2}	3.6600(10)
Cs1–S1	3.9797(9)	Cs2–Br1^{9}	3.7303(5)
Cs1–S2	3.5716(9)	Cs2–Br1^{8}	3.8560(5)
Cs1–S2^{2}	3.7193(9)	Cs2–Br2^{7}	3.7268(4)
Cs1–S3^{3}	3.6784(9)	Cs2–Br2^{4}	3.6507(4)
Br2—In—S11	91.60(2)	S4—P—Cs1	160.07(4)
Br2—In—S1	163.89(2)	S4—P—Cs2^{2}	87.47(4)
Br1—In—Br2	96.333(14)	S3—P—Cs1	87.33(4)
Br1—In—S11	165.991(19)	S3—P—Cs2^{2}	160.04(4)
Br1—In—S1	90.28(2)	S3—P—S4	112.49(5)
S1—In—S11	85.12(3)	In—Br1—Cs1^{8}	94.016(12)
S41—In—Br2	102.28(3)	In—Br1—Cs1	101.886(13)
S41—In—Br1	91.99(2)	In—Br1—Cs2^{12}	94.679(12)
S4^{1}—In—S1^{1}	75.00(3)	In—Br1—Cs2^{3}	149.359(14)
S4^{1}—In—S1	92.11(3)	Cs1^{8}—Br1—Cs1	99.971(10)
S4^{1}—In—S3	161.96(3)	Cs1—Br1—Cs2^{3}	106.866(10)
S3—In—Br2	88.92(2)	Cs1^{8}—Br1—Cs2^{12}	158.497(13)
S3—In—Br1	100.87(3)	Cs1^{8}—Br1—Cs2^{3}	91.283(11)
S3—In—S11	90.78(3)	Cs1—Br1—Cs2^{12}	97.422(10)

S3—In—S1	75.39(3)	$Cs2^{3}$—Br1—$Cs2^{12}$	71.533(9)
$Cs2^{2}$—P—Cs1	72.726(14)	In—Br2—$Cs1^{10}$	98.623(12)
S1—P—Cs1	70.83(3)	In—Br2—$Cs1^{8}$	92.260(12)
S1—P—$Cs2^{2}$	68.46(3)	In—Br2—$Cs2^{11}$	97.642(12)
S1—P—S4	104.47(5)	In—Br2—$Cs2^{8}$	155.222(15)
S1—P—S3	104.69(5)	$Cs1^{8}$—Br2—$Cs1^{10}$	95.971(10)
S2—P—Cs1	59.39(3)	$Cs1^{8}$—Br2—$Cs2^{11}$	162.193(12)
S2—P—$Cs2^{2}$	60.71(3)	$Cs2^{8}$—Br2—$Cs1^{8}$	91.001(10)
S2—P—S1	116.10(5)	$Cs2^{11}$—Br2—$Cs1^{10}$	97.123(11)
S2—P—S4	109.07(5)	$Cs2^{8}$—Br2—$Cs1^{10}$	105.452(11)
S2—P—S3	109.96(5)	$Cs2^{8}$—Br2—$Cs2^{11}$	73.900(9)

Symmetry codes: (1)1-*X*,1-*Y*,1-*Z*; (2)1/2-*X*, -1/2+*Y*,1/2-*Z*; (3)3/2-*X*, -1/2+*Y*,1/2-*Z*; (4)+*X*,-1+*Y*,+*Z*; (5)1-*X*,1-*Y*,-*Z*; (6)1/2-*X*,1/2+*Y*,1/2-*Z*; (7)-1/2+*X*,3/2-*Y*,-1/2+*Z*; (8)3/2-*X*,1/2+*Y*,1/2-*Z*; (9)-1/2+*X*,1/2-*Y*,-1/2+*Z*; (10)+*X*,1+*Y*,+*Z*; (11)1/2+*X*,3/2-*Y*,1/2+*Z*; (12)1/2+*X*,1/2-*Y*,1/2+*Z*

5. Fig. S1

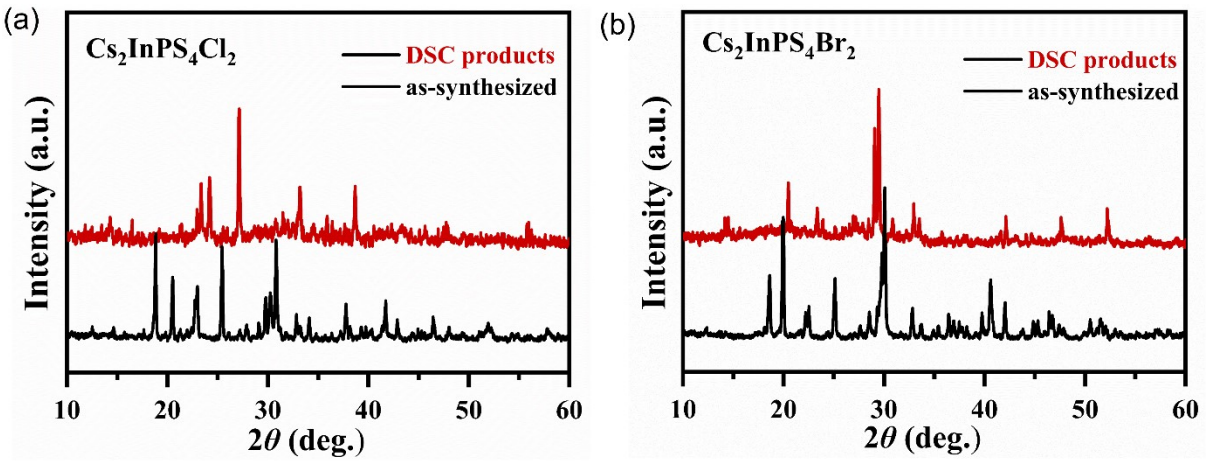

Fig. S1. Powder X-ray diffraction patterns of $Cs_2InPS_4X_2$ (X = Cl, Br): as-synthesized (black), and DSC products (red).