Supporting Information

Broadband Infrared-Transparent Crystals Enabled by Heterologous Isomorphic Substitution

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Experimental Section

Synthesis

The following starting materials are commercially available and used without additional purification: ZnI_2 (99%, Macklin), $ZnCl_2$ (99%, Macklin), RbCl (99.5%, Aladdin), KCl (99%, Aladdin), and NH_4Cl (99%, Aladdin). The three compounds were successfully synthesized using a mild aqueous solution method, with the following stoichiometric ratios: RbCl (0.7256 g, 6 mmol), $ZnCl_2$ (0.1363 g, 1 mmol), ZnI_2 (0.3192 g, 1 mmol), and 20 mL of deionized water were used to prepare Rb_3ZnCl_4I; KCl (0.4474 g, 3 mmol), $ZnCl_2$ (0.1363 g, 1 mmol), ZnI_2 (0.3192 g, 1 mmol), and 20 mL of deionized water were used to prepare K_3ZnCl_4I; NH_4Cl (0.3209 g, 3 mmol), $ZnCl_2$ (0.1363 g, 1 mmol), ZnI_2 (0.3192 g, 1 mmol), and 20 mL of deionized water to prepare $(NH_4)_3ZnCl_4I$; Place the above ingredients in a beaker, add 20 mL of deionized water, place on a 50 °C hot plate, and stir for 10 minutes until completely dissolved; After the reaction was complete, the pH was maintained at around 6.0. The solution was filtered hot through filter paper using a preheated funnel to remove insoluble impurities and dust, yielding a clear hot solution. The beaker was then covered with plastic wrap, into which 10-15 small holes were punctured, and left at room temperature to evaporate for approximately two weeks, resulting in crystals of the three compounds.

Single Crystal Structure Data Collection.

The single-crystal XRD data were collected on a Bruker D8 Venture diffractometer using Mo Kα radiation (λ = 0.71073 Å) at room temperature. Data integration, cell refinement and absorption corrections of the data were completed by utilizing SAINT program.[1] The structure was solved with Olex2 and SHELXTL by direct methods.[2] All the atom positions were refined using full matrix least squares techniques, the final least squares refinement is on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$. The structure was checked for missing symmetry elements by the program PLATON,[3] and no higher symmetries were found. Relevant crystallographic data are listed in Table S1.

Powder X-ray Diffraction

The powder X-ray diffraction data was collected using a Bruker D2 PHASER diffractometer. The recorded 2θ patterns from 10 to 70° with a counting rate of 1 s per step and a scanning step width of 0.02 ° were selected. The purity of the polycrystalline was confirmed by powder X-ray diffraction, and the experimental pattern agrees well with the calculated result (Figure S2).

Thermal Analysis

The thermal gravimetric (TG) analysis and differential scanning calorimetry (DSC) of A_3ZnCl_4I (A = K, Rb, and NH_4) were carried out on a simultaneous NETZSCH STA 449C thermal analyzer instrument to evaluate the thermal stability of the compounds. The powder samples were placed into a Pt crucible and heated from 40 to 600 ℃ at a rate of 5 °C·min^{-1} under a flowing of N_2 atmosphere. TG-DSC curves of A_3ZnCl_4I (A = K, Rb, and NH_4) were obtained, and calcination experiments were performed based on the corresponding peak temperatures.

UV-vis-NIR transmittance spectra Measurement

The UV-Vis-IR transmittance spectra data for the single-crystal of A_3ZnCl_4I (A = K, Rb, and NH_4) were collected using a Shimadzu SolidSpec-3700DUV spectrophotometer with the measurement range extending from 200 to 1400 nm.

Calculation details

The theoretical calculations of all the title compounds were performed with the plane-wave pseudopotential method implemented in the CASTEP, and the electronic structures of reported series were determined based on density functional theory (DFT).[4]The optimized norm-conserving pseudopotentials were used to simulate ion–electron interactions for all the constituent elements in reported compounds. The exchange and correlation effects were treated by the Perdew–Burke–Ernzerhof (PBE) method in generalized gradient approximation (GGA).[5-6] The kinetic energy cutoffs and Monkhorst–Pack k-point meshes of all compounds were set as 830 eV. The Monkhorst–Pack k-point meshes of compounds were set as 4×2×3.

Table S1. Crystal data and structure refinement parameters of Rb_3ZnCl_4I, K_3ZnCl_4I, and $(NH_4)_3ZnCl_4I$.

Empirical formula	Rb_3ZnCl_4I	K_3ZnCl_4I	$(NH_4)_3ZnCl_4I$
Formula weight	590.48	451.37	388.20
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Cmcm*	*Cmcm*	*Cmcm*
a/Å	7.1693(5)	7.0381(4)	7.1178(5)
b/Å	16.8387(12)	16.4906(13)	16.7739(9)
c/Å	10.0487(7)	9.6952(6)	9.9227(5)
α/°	90	90	90
Volume/Å^3	1213.10(15)	1125.25(13)	1184.70(12)
Z	4	4	4
ρ_{calc}g/cm^3	3.233	2.664	2.176
μ/mm^{-1}	17.345	6.915	5.527
F(000)	1048.0	832.0	736.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2*θ* range for data collection/°	4.838 to 55.146	4.94 to 55.042	6.218 to 54.988
Index ranges	-9 ≤ h ≤ 9,-21 ≤ k ≤ 21, -13 ≤ l ≤ 13	-9 ≤ h ≤ 9, -21 ≤ k ≤ 21, -12 ≤ l ≤ 12	-9 ≤ h ≤ 9, -21 ≤ k ≤ 21, -12 ≤ l ≤ 12
Reflections collected	11529	12218	11595
Independent reflections	796 [R_{int} = 0.0420, R_{sigma} = 0.0218]	745 [R_{int} = 0.0377, R_{sigma} = 0.0154]	778 [R_{int} = 0.0372, R_{sigma} = 0.0171]
Data/restraints/parameters	796/0/32	745/0/32	778/78/55
Goodness-of-fit on F^2	1.096	1.093	1.147
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0178, wR_2 = 0.0414	R_1 = 0.0121, wR_2 = 0.0281	R_1 = 0.0194, wR_2 = 0.0561
Final *R* indexes [all data]	R_1 = 0.0185, wR_2 = 0.0418	R_1 = 0.0128, wR_2 = 0.0283	R_1 = 0.0203, wR_2 = 0.0566
Largest diff. peak/hole / e Å^{-3}	0.70/-0.47	0.46/-0.29	0.58/-0.52

[a] $R_1 = \sum||F_o| - |Fc||/\sum|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S2. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and BVS results for Rb_3ZnCl_4I. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)	BVS
Rb1	10000	6572.4(2)	9832.7(3)	39.38(11)	0.95
Rb2	5000	5563.2(2)	2500	32.69(12)	1.15
Zn1	5000	6839.4(3)	7500	25.71(13)	2.06
Cl1	5000	6140.3(5)	5600.7(8)	46.5(2)	0.99
Cl2	7537.2(9)	7648.1(4)	7500	37.27(18)	1.03
I1	10000	4946.2(2)	7500	36.01(11)	1.03

Table S3. Bond lengths for Rb_3ZnCl_4I

Atom1	Atom2	Bond length	Atom1	Atom2	Bond length
Rb1	Cl1[3]	3.9281(10)	Rb2	Cl1[9]	3.4453(10)
Rb1	Cl1[4]	3.6836(3)	Rb2	Cl1[10]	3.4453(10)
Rb1	Cl1[5]	3.6836(3)	Rb2	Cl1	3.2638(8)
Rb1	Cl2	3.4486(6)	Rb2	Cl1[11]	3.2638(8)
Rb1	Cl2[6]	3.4951(6)	Rb2	Cl2[12]	3.4914(8)
Rb1	Cl2[2]	3.4951(6)	Rb2	Cl2[13]	3.4914(8)
Rb1	Cl2[7]	3.4486(6)	Rb2	I1[9]	3.6859(3)
Rb1	I1	3.6046(4)	Rb2	I1[14]	3.6859(3)
Rb1	I1[8]	3.7045(4)	Zn1	Cl1[5]	2.2424(8)
Zn1	Cl2	2.2722(7)	Zn1	Cl1	2.2424(8)
Zn1	Cl2[15]	2.2722(7)			

[1]1+X,+Y,+Z; [2]3/2-X,3/2-Y,2-Z; [3]3/2-X,3/2-Y,1/2+Z; [4]1+X,+Y,3/2-Z; [5]+X,+Y,3/2-Z; [6]2-X,+Y,3/2-Z; [7]1/2+X,3/2-Y,1/2+Z; [8]2-X,1-Y,2-Z; [9]1-X,1-Y,1-Z; [10]+X,+Y,1/2-Z; [11]1-X,1-Y,-1/2+Z; [12]-1/2+X,3/2-Y,-1/2+Z; [13]3/2-X,3/2-Y,1-Z; [14]2-X,1-Y,1-Z; [15]1-X,+Y,3/2-Z

Table S4. The angles for Rb_3ZnCl_4I.

Atom1	Atom2	Atom3	Angle/°	Atom1	Atom2	Atom3	Angle/°
Cl1[5]	Rb1	Cl1[3]	102.529(15)	Cl2[15]	Rb2	Cl2[14]	60.76(2)
Cl1[5]	Rb1	Cl1[4]	153.38(3)	Cl2[14]	Rb2	I1[16]	133.836(15)
Cl1[4]	Rb1	Cl1[3]	102.529(15)	Cl2[14]	Rb2	I1[11]	73.079(13)
Cl1[5]	Rb1	I1[6]	87.086(13)	Cl2[15]	Rb2	I1[11]	133.836(15)
Cl1[4]	Rb1	I1[6]	87.086(13)	Cl2[15]	Rb2	I1[16]	73.079(13)
Cl2[8]	Rb1	Cl1[5]	132.170(18)	I1[11]	Rb2	I1[16]	153.085(15)
Cl2[2]	Rb1	Cl1[3]	58.742(15)	Cl1[5]	Zn1	Cl1	116.67(5)
Cl2[7]	Rb1	Cl1[4]	61.651(17)	Cl1	Zn1	Cl2[20]	108.337(15)
Cl2[7]	Rb1	Cl1[3]	67.578(15)	Cl1[5]	Zn1	Cl2[20]	108.337(15)
Cl2[8]	Rb1	Cl1[3]	58.742(15)	Cl1[5]	Zn1	Cl2	108.338(15)
Cl2	Rb1	Cl1[4]	121.442(17)	Cl1	Zn1	Cl2	108.337(15)
Cl2	Rb1	Cl1[5]	61.651(17)	Cl1[11]	Rb2	Cl2[14]	135.909(12)
Cl2[7]	Rb1	Cl1[5]	121.442(17)	Cl1[13]	Rb2	Cl2[15]	75.116(16)
Cl2[2]	Rb1	Cl1[5]	70.026(17)	Cl1[12]	Rb2	Cl2[14]	135.909(12)
Cl2[2]	Rb1	Cl1[4]	132.170(18)	Cl1[12]	Rb2	Cl2[15]	135.909(12)
Cl2[8]	Rb1	Cl1[4]	70.026(17)	Cl1	Rb2	Cl2[15]	75.116(16)
Cl2	Rb1	Cl1[3]	67.578(15)	Cl1[11]	Rb2	Cl2[15]	135.909(12)
Cl2	Rb1	Cl2[2]	93.299(7)	Cl1[13]	Rb2	I1[16]	93.973(4
Cl2[7]	Rb1	Cl2[2]	126.191(10)	Cl1[11]	Rb2	I1[16]	78.828(7)
Cl2[8]	Rb1	Cl2[2]	62.72(2)	Cl1[13]	Rb2	I1[11]	93.973(4)
Cl2[7]	Rb1	Cl2	61.59(2)	Cl1[12]	Rb2	I1[16]	78.828(7)
Cl2	Rb1	Cl2[8]	126.191(10)	Cl1	Rb2	I1[16]	93.973(4)
Cl2[7]	Rb1	Cl2[8]	93.299(7)	Cl1	Rb2	I1[11]	93.973(4)
Cl2[8]	Rb1	I1	141.628(13)	Cl1[12]	Rb2	I1[11]	78.828(7)
Cl2[2]	Rb1	I1[6]	72.807(13)	Cl1[11]	Rb2	I1[11]	78.828(7)
Cl2[2]	Rb1	I1	141.628(13)	Cl1[13]	Rb2	Cl1[11]	140.96(2)
Cl2[7]	Rb1	I1[6]	148.687(11)	Cl1	Rb2	Cl1[13]	145.36(4)
Cl2	Rb1	I1[6]	148.687(11)	Cl1	Rb2	Cl1[12]	140.96(2)
Cl2[7]	Rb1	I1	87.533(13)	Cl1[13]	Rb2	Cl1[12]	73.68(2)
Cl2	Rb1	I1	87.533(13)	Cl1	Rb2	Cl1[11]	73.68(2)
Cl2[8]	Rb1	I1[6]	72.807(13)	Cl1[12]	Rb2	Cl1[11]	67.28(3)
I1	Rb1	Cl1[5]	76.881(15)	Cl1	Rb2	Cl2[14]	75.116(16)
I1	Rb1	Cl1[4]	76.881(15)	Cl1[13]	Rb2	Cl2[14]	75.116(16)
I1[6]	Rb1	Cl1[3]	122.325(15)	I1	Rb1	I1[6]	86.910(9)
I1	Rb1	Cl1[3]	150.766(16)				

[1]1+X,+Y,+Z; [2]3/2-X,3/2-Y,2-Z; [3]3/2-X,3/2-Y,1/2+Z; [4]+X,+Y,3/2-Z; [5]1+X,+Y,3/2-Z; [6]2-X,1-Y,2-Z; [7]1/2+X,3/2-Y,1/2+Z; [8]2-X,+Y,3/2-Z; [9]-1+X,+Y,-1+Z; [10]+X,+Y,-1+Z; [11]1-X,1-Y,1-Z; [12]+X,+Y,1/2-Z; [13]1-X,1-Y,-1/2+Z; [14]3/2-X,3/2-Y,1-Z; [15]-1/2+X,3/2-Y,-1/2+Z; [16]2-X,1-Y,1-Z; [17]-1+X,+Y,3/2-Z; [18]3/2-X,3/2-Y,-1/2+Z; [19]-1+X,+Y,+Z; [20]1-X,+Y,3/2-Z; [21]2-X,1-Y,-1/2+Z

Table S5. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and BVS results for K_3ZnCl_4I. U_{eq} is defined as 1/3 of the trace of the orthogonalised U tensor.

Atom	*x*	*y*	*z*	U(eq)	BVS
K1	0	3442.7(3)	160.1(5)	47.90(13)	0.85
K2	5000	4445.4(4)	7500	37.12(15)	1.04
Zn1	5000	3178.0(2)	2500	26.79(9)	2.11
Cl1	5000	3902.1(4)	4446.2(5)	56.69(18)	0.99
Cl2	2438.0(7)	2348.9(3)	2500	45.78(14)	0.98
I1	0	5048.9(2)	2500	38.16(8)	0.96

Table S6. Bond lengths for K_3ZnCl_4I

Atom1	Atom2	Bond length	Atom1	Atom2	Bond length
K1	Cl2	3.3682(6)	K2	Cl1[14]	3.3145(8)
K1	Cl2[15]	3.3682(6)	Zn1	Cl2[8]	2.2629(5)
K1	Cl2[7]	3.4069(6)	Zn1	Cl2	2.2629(5)
K1	Cl2[16]	3.4069(6)	Zn1	Cl1	2.2330(6)
K1	Cl1[17]	3.6199(3)	Zn1	Cl1[5]	2.2330(5)
K1	Cl1[5]	3.6199(3)	I1	K2[1]	3.6165(2)
K2	Cl2[11]	3.4204(8)	I1	K2[2]	3.6165(2)
K2	Cl2[12]	3.4204(8)	I1	K1[3]	3.5831(6)
K2	Cl1[1]	3.3145(8)	I1	K1	3.4874(5)
K2	Cl1[13]	3.0933(6)	I1	K1[4]	3.5831(6)
K2	Cl1	3.0933(6)	I1	K1[5]	3.4874(5)

[1]1-X,1-Y,1-Z; [2]-X,1-Y,1-Z; [3]+X,+Y,1/2-Z; [4]-X,1-Y,-Z; [5]-X,1-Y,1/2+Z; [6]1/2-X,1/2-Y,-Z; [7]1/2-X,1/2-Y,1/2+Z; [8]1-X,+Y,1/2-Z; [9]1+X,+Y,1+Z; [10]+X,+Y,1+Z; [11]1/2-X,1/2-Y,1-Z; [12]1/2+X,1/2-Y,1/2+Z; [13]+X,+Y,3/2-Z; [14]1-X,1-Y,1/2+Z; [15]-1/2+X,1/2-Y,-1/2+Z; [16]-X,+Y,1/2-Z; [17]-1+X,+Y,1/2-Z

Table S7. The angles for K_3ZnCl_4I.

Atom1	Atom2	Atom3	Angle/°	Atom1	Atom2	Atom3	Angle/°
Cl2[8]	Zn1	Cl2	105.66(3)	Cl1	K2	Cl1[13]	141.53(2)
Cl1[4]	Zn1	Cl2	108.852(11)	Cl1	K2	Cl1[1]	72.137(19)
Cl1	Zn1	Cl2[8]	108.851(11)	Cl1[13]	K2	Cl1[1]	69.40(2)
Cl1[4]	Zn1	Cl2[8]	108.851(11)	Cl1[14]	K2	Cl1[13]	72.136(19)
Cl1	Zn1	Cl2	108.851(11)	Cl1[14]	K2	Cl1[1]	141.53(2)
Cl1	Zn1	Cl1[4]	115.34(4)	I1	K1	I1[3]	86.617(13)
I1[1]	K2	I1[2]	153.34(2)	I1[3]	K1	Cl1[17]	86.022(12)
Cl2[11]	K2	I1[2]	133.442(18)	I1	K1	Cl1[4]	76.847(12)
Cl2[12]	K2	I1[1]	133.442(18)	I1[3]	K1	Cl1[4]	86.022(12)
Cl2[12]	K2	I1[2]	73.222(11)	I1	K1	Cl1[17]	76.847(12)
Cl2[11]	K2	I1[1]	73.222(11)	Cl2[18]	K1	I1	88.200(14)
Cl2[12]	K2	Cl2[11]	60.22(2)	Cl2	K1	I1[3]	148.935(10)
Cl1	K2	I1[1]	93.829(3)	Cl2[7]	K1	I1[3]	73.808(13)
Cl1[1]	K2	I1[1]	79.071(9)	Cl2	K1	I1	88.201(14)
Cl1[1]	K2	I1[2]	79.071(9)	Cl2[19]	K1	I1[3]	73.808(13)
Cl1[13]	K2	I1[2]	79.071(9)	Cl2[19]	K1	I1	141.579(13)
Cl1	K2	I1[2]	93.829(3)	Cl2[7]	K1	I1	141.579(13)
Cl1[14]	K2	I1[1]	93.829(3)	Cl2[18]	K1	I1[3]	148.935(9)
Cl1[14]	K2	I1[2]	93.829(3)	Cl2	K1	Cl2[7]	92.006(9)
Cl1[13]	K2	I1[1]	79.071(9)	Cl2	K1	Cl2[19]	125.049(16)
Cl1[13]	K2	Cl2[12]	135.334(9)	Cl2[19]	K1	Cl2[7]	63.913(17)
Cl1[14]	K2	Cl2[12]	75.491(16)	Cl2[18]	K1	Cl2	61.253(18)
Cl1[14]	K2	Cl2[11]	75.491(16)	Cl2[18]	K1	Cl2[19]	92.007(9)
Cl1[13]	K2	Cl2[11]	135.334(9)	Cl2[18]	K1	Cl2[7]	125.050(16)
Cl1[1]	K2	Cl2[11]	135.334(9)	Cl2[7]	K1	Cl1[17]	132.420(17)
Cl1[1]	K2	Cl2[12]	135.334(9)	Cl2[18]	K1	Cl1[17]	62.986(13)
Cl1	K2	Cl2[12]	75.490(16)	Cl2[19]	K1	Cl1[4]	132.420(17)
Cl1	K2	Cl2[11]	75.490(16)	Cl2	K1	Cl1[4]	62.986(13)
Cl1	K2	Cl1[14]	146.33(3)	Cl2[18]	K1	Cl1[4]	122.432(17)
Cl2	K1	Cl1[17]	122.432(17)	Cl2[7]	K1	Cl1[4]	69.237(13)
Cl1[4]	K1	Cl1[17]	152.89(3)	Cl2[19]	K1	Cl1[17]	69.237(13)

[1]1-X,1-Y,1-Z; [2]-X,1-Y,1-Z; [3]+X,+Y,1/2-Z; [4]-X,1-Y,-Z; [5]-X,1-Y,1/2+Z; [6]1/2-X,1/2-Y,1/2+Z; [7]1/2-X,1/2-Y,-Z; [8]1-X,+Y,1/2-Z; [9]1+X,+Y,1+Z; [10]+X,+Y,1+Z; [11]1/2+X,1/2-Y,1/2+Z; [12]1/2-X,1/2-Y,1-Z; [13]1-X,1-Y,1/2+Z; [14]+X,+Y,3/2-Z; [15]+X,+Y,-1+Z; [16]-1+X,+Y,-1+Z; [17]-1+X,+Y,1/2-Z; [18]-X,+Y,1/2-Z; [19]-1/2+X,1/2-Y,-1/2+Z; [20]1+X,+Y,1/2-Z

Table S8. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and BVS results for $(NH_4)_3ZnCl_4I$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U tensor.

Atom	x	y	z	U(eq)	BVS
N1	5000	3440.5(19)	4807(3)	45.1(8)	-
N2	10000	5539(3)	2500	36.9(9)	-
Zn1	10000	3145.4(3)	2500	27.51(16)	2.05
Cl1	7455.0(12)	2329.3(5)	2500	41.6(2)	-
Cl2	10000	3862.0(6)	4408.5(8)	50.6(3)	-
I1	5000	5062.4(2)	2500	41.58(15)	-

Table S9. Bond lengths for $(NH_4)_3ZnCl_4I$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	Cl1	2.2706(9)	Zn1	Cl2	2.2430(9)
Zn1	Cl1[1]	2.2705(9)	Zn1	Cl2[2]	2.2430(9)

[1]2-X,+Y,1/2-Z; [2]+X,+Y,1/2-Z

Table S10. The angles for $(NH_4)_3ZnCl_4I$

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1[1]	Zn1	Cl1	105.85(5)	Cl2[2]	Zn1	Cl1[1]	108.850(18)
Cl2	Zn1	Cl1	108.851(18)	Cl2[2]	Zn1	Cl1	108.851(17)
Cl2	Zn1	Cl1[1]	108.850(18)	Cl2[2]	Zn1	Cl2	115.19(6)

[1]2-X,+Y,1/2-Z; [2]+X,+Y,1/2-Z

Figure S1. The experimental and calculated PXRD patterns of (a) Rb_3ZnCl_4I, (b) K_3ZnCl_4I, and (c) $(NH_4)_3ZnCl_4I$. Among them, the crystals of Rb_3ZnCl_4I and K_3ZnCl_4I were exposed to the air for two months, and the crystal of $(NH_4)_3ZnCl_4I$ was exposed to the air for one week.

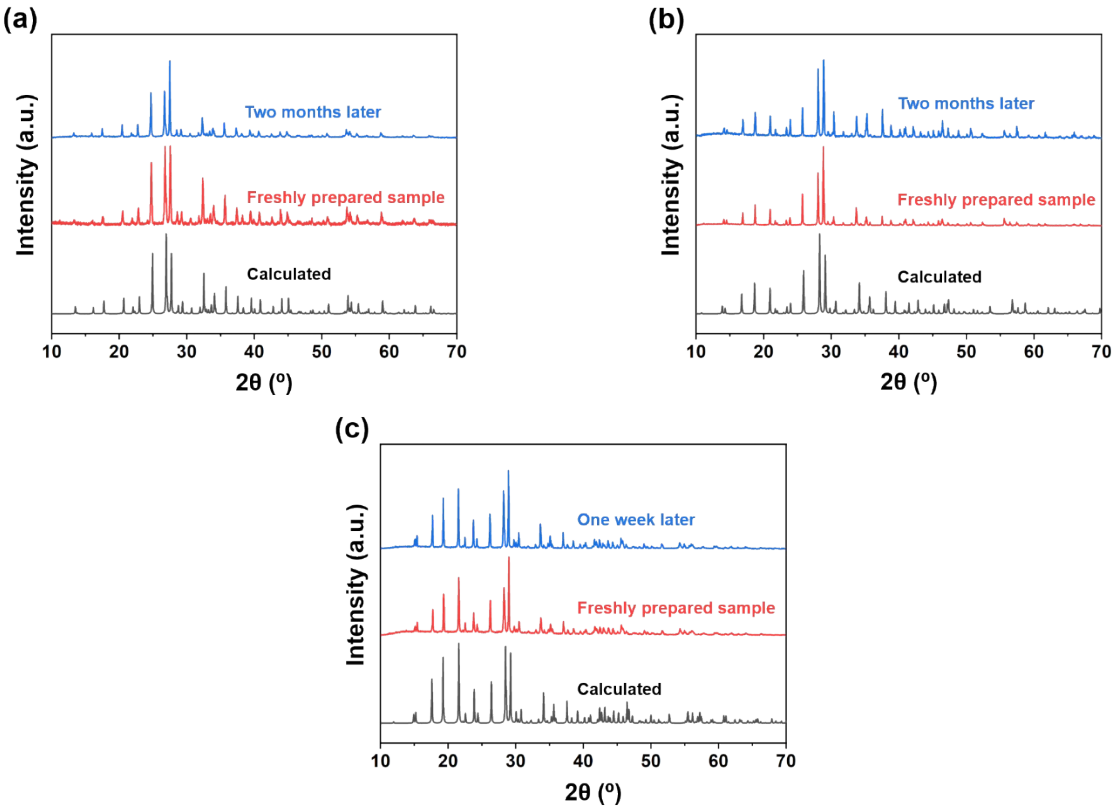


Figure S2. (a) $Ba(1)S_7I_2$ and $Ba(2)S_6I_2$ ligands and $[GaS_4]$ anion units. (b) Overall structure of Ba_3GaS_4I. (c) Layer formed by interconnected $[Ba(1)S_7I_2]$ units along the a-axis. (d) Ba(1) atoms form parallel chains around S atoms. (e) Layer formed by interconnected $[Ba(2)S_6I_2]$ units along the a-axis. (f) Ba(2) atoms connect via S atoms to form zigzag chains.

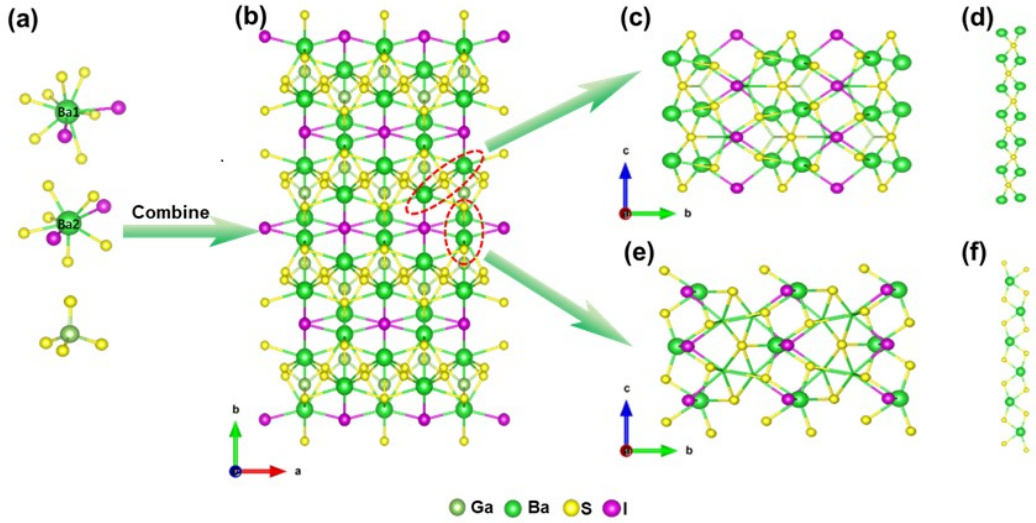


Figure S3. The band structure of (a) Rb_3ZnCl_4I, (b) K_3ZnCl_4I, (c) $(NH_4)_3ZnCl_4I$, and (d) Ba_3GaS_4I with GGA method.

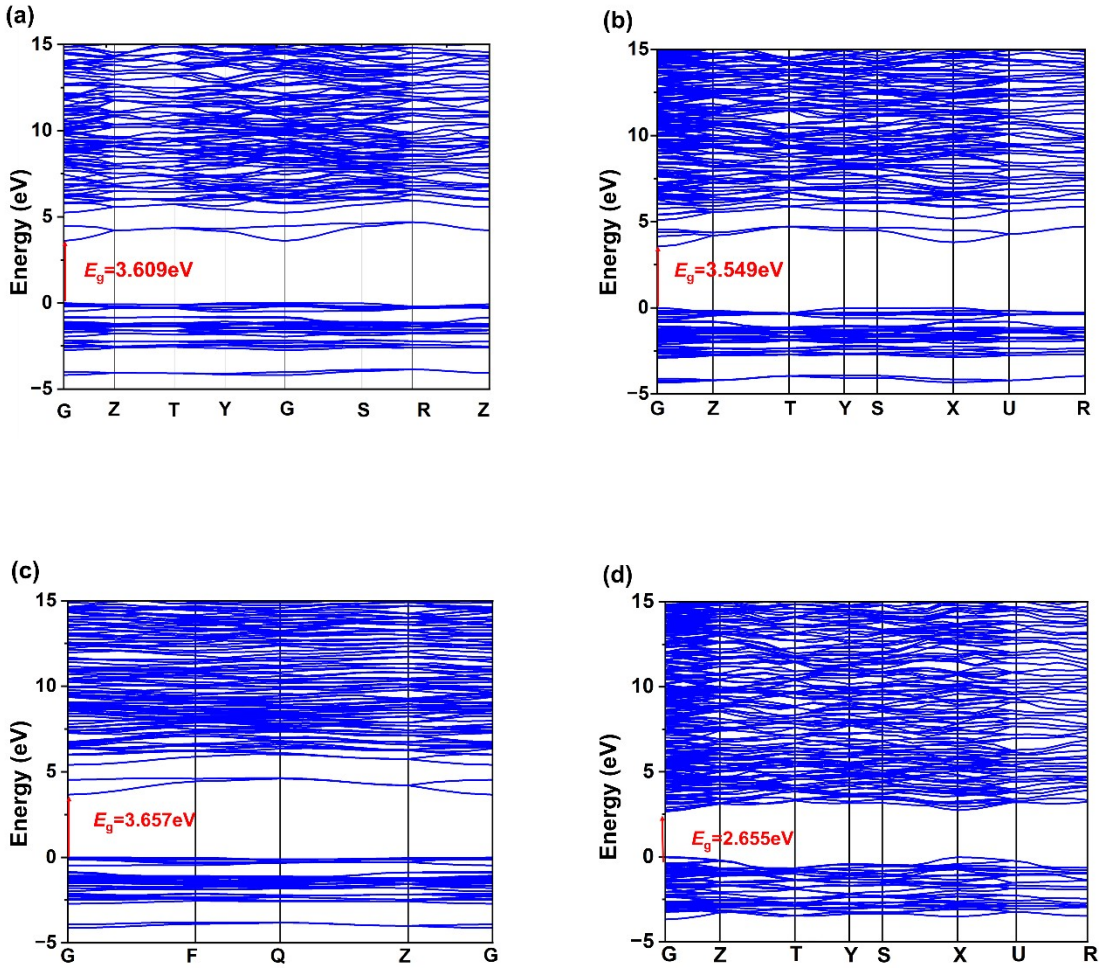


Figure S4. PDOS of (a) Rb_3ZnCl_4I, (b) K_3ZnCl_4I, (c) $(NH_4)_3ZnCl_4I$, and (d) Ba_3GaS_4I.

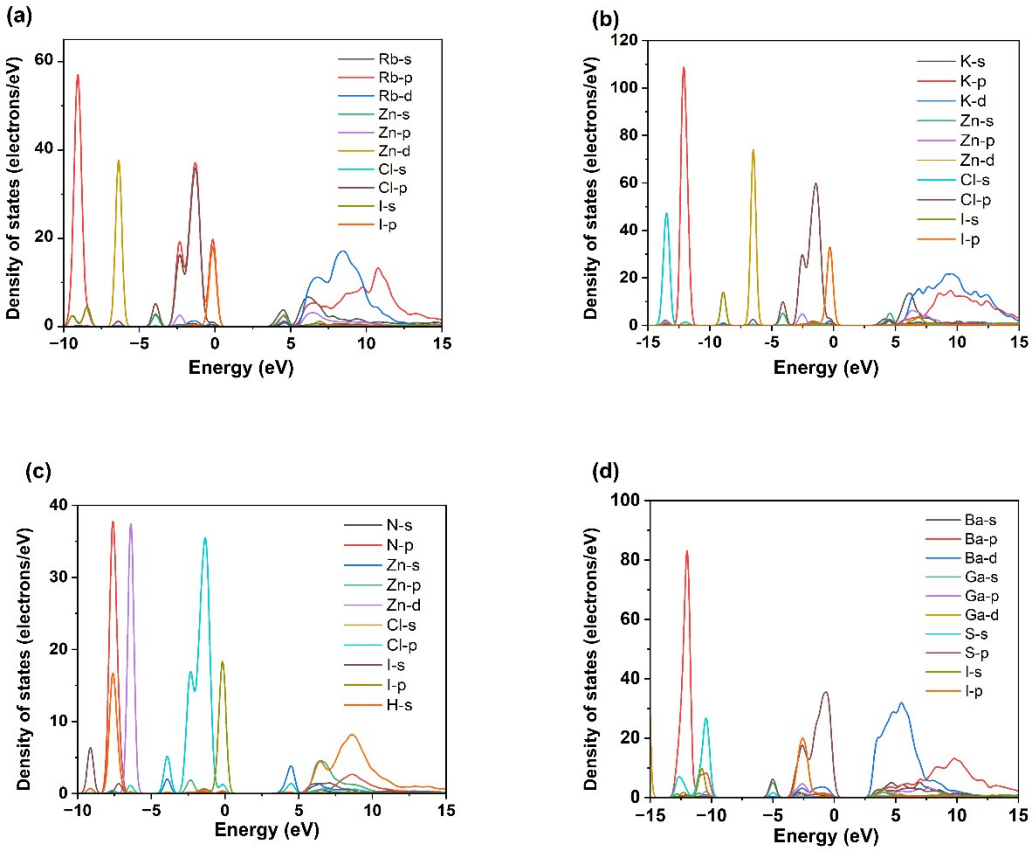


Figure S5. Calculated birefringence of (a) Rb_3ZnCl_4I, (b) K_3ZnCl_4I, and (c) $(NH_4)_3ZnCl_4I$.

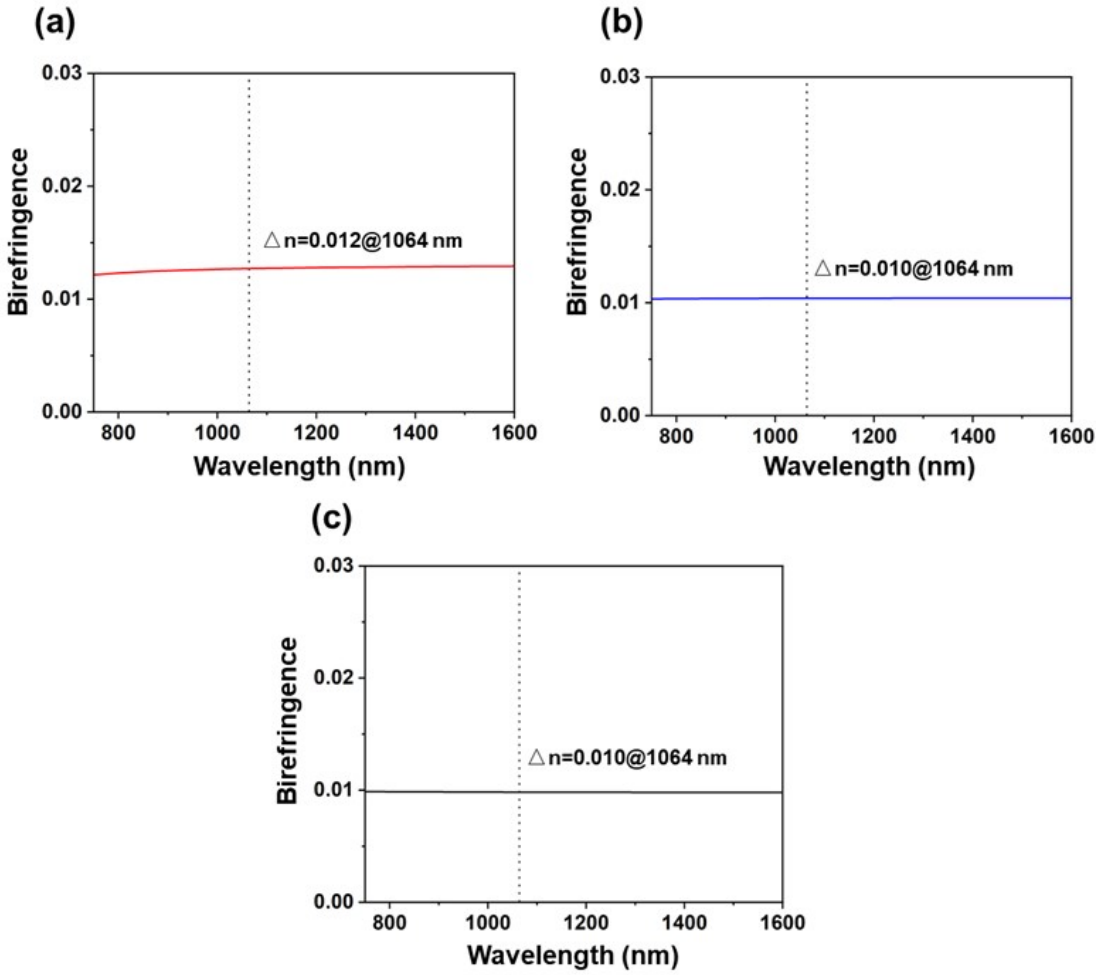


Figure S6. Calculated infrared (IR) absorption spectra of (a) Rb_3ZnCl_4I, (b) K_3ZnCl_4I, (c) $(NH_4)_3ZnCl_4I$, and (d) Ba_3GaS_4I.

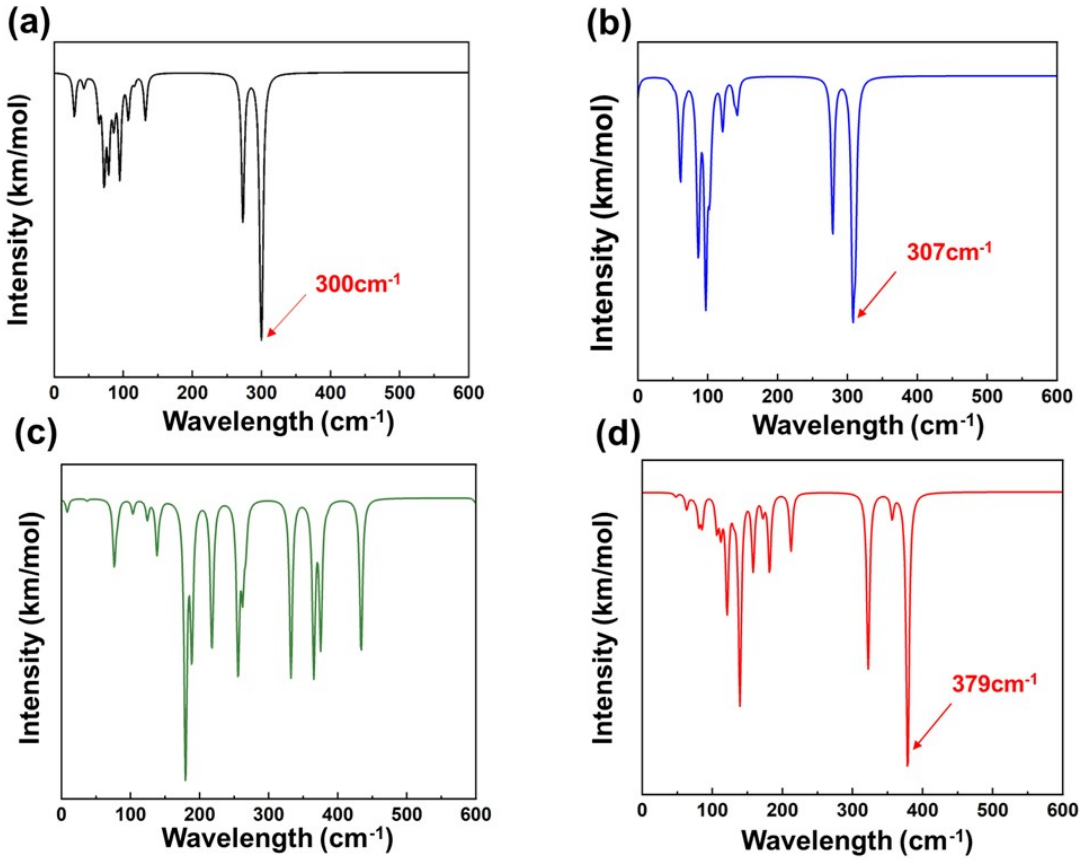


Figure S7. FT-IR spectrum of $(NH_4)_3ZnCl_4I$.

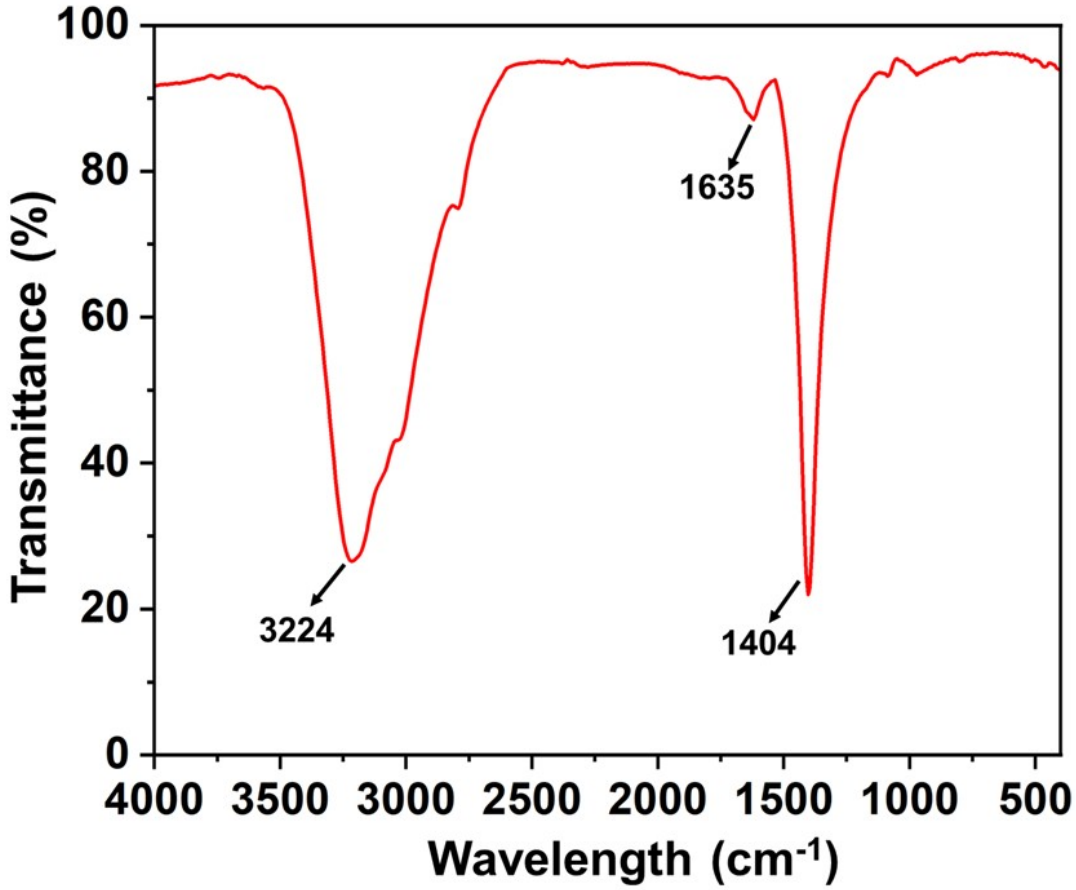
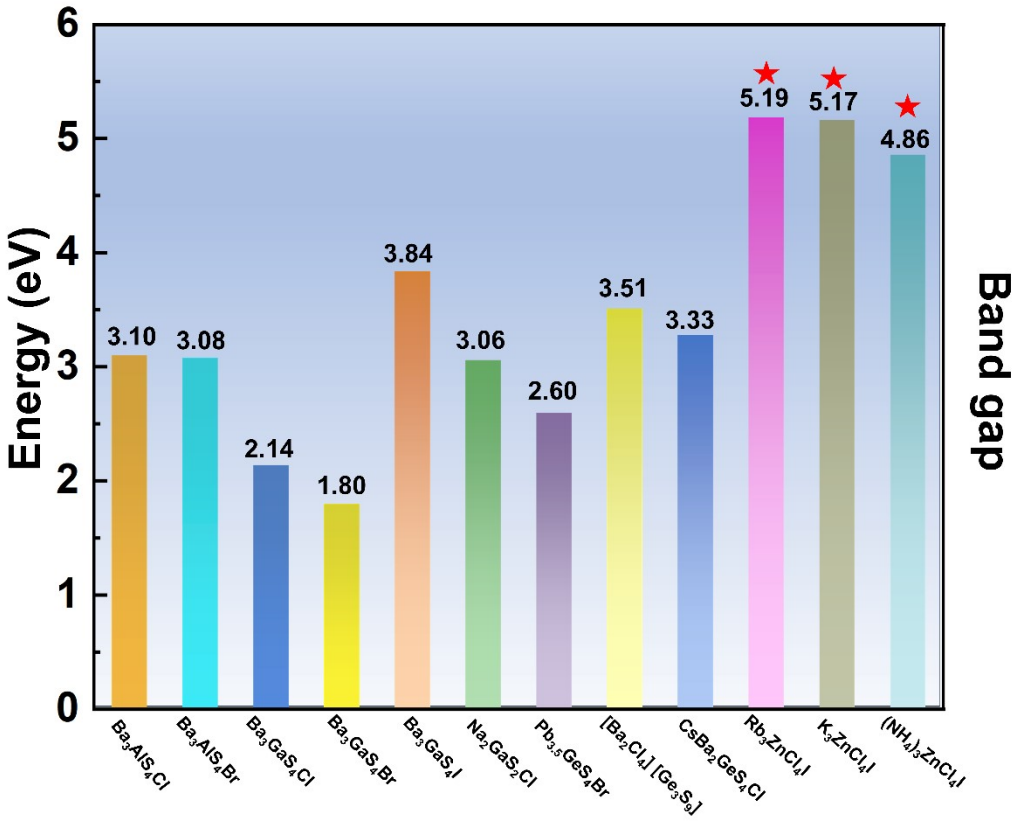


Figure S8. A bandgap comparison compounds containing chalcogenic tetrahedral units



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