# $CsAB_8O_{12}F_2 \cdot CsI$ (A = K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>): Design of Two Fluorooxoborates with

# **Benign Layered Structures via Salt-Inclusion Strategy**

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#### **EXPERIMENTAL SECTION**

#### Synthesis and Crystal Growth

Single crystals of CKBFI and CNBFI were obtained by high-temperature solution method in a closed system, based on the following reaction:  $2CsF + KI + 4B_2O_3 = CsKB_8O_{12}F_2 \cdot CsI$  (CKBFI);  $2CsF + NH_4I + 4B_2O_3 = CsNH_4B_8O_{12}F_2 \cdot CsI$  (CNBFI). The compositions of respective mixtures are as follows: CsF (0.304 g, 2 mmol), KI (0.166 g, 1 mmol) and  $B_2O_3$  (0.278 g, 4 mmol) for (CKBFI); CsF (0.304 g, 2 mmol), NH\_4I (0.145 g, 1 mmol), and  $B_2O_3$  (0.278 g, 4 mmol) for (CNBFI); The mixtures were thoroughly ground, placed in separate quartz tubes (the inner diameter is 10 mm), and tubes were flame-sealed under  $10^{-3}$  Pa. The tubes were heated to 430 °C in 10 h, held at this temperature for 10 h, and cooled to room temperature with a rate of 1 °C·h<sup>-1</sup>. Then, the CKBFI and CNBFI crystals can be obtained. The as-grown CKBFI crystal with dimensions up to 2 × 2 × 0.5 mm<sup>3</sup> is shown in Figure 3a.

Polycrystalline samples of CKBFI can be obtained by high-temperature solid-state reaction. A mixture of CsF, CsI, KBF<sub>4</sub>, and B<sub>2</sub>O<sub>3</sub> in the stoichiometric ratio was sealed in a quartz tube (the inner diameter is 10 mm). The tube was heated at 430 °C for 48 h and cooled to room temperature at a rate of 1 °C·h<sup>-1</sup>. Figure S4 shows the experimental and simulated patterns from the single crystal data of CKBFI. The observed PXRD patterns are in good agreement with the corresponding theoretical ones, which further confirms the validity of structural models.

#### Single-crystal X-ray Crystallography

The single-crystal XRD data of CKBFI and CNBFI were collected with a Bruker D8 Venture single-crystal diffractometer using Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 293(2) K, respectively. We used the Bruker SAINT program to carry out the data integration and absorption corrections,<sup>1</sup> and analyzed the single-crystal data using the Olex2<sup>2</sup> program. The crystal structures were solved by the Intrinsic Phasing method and refined by the SHELXL least-squares refinement package.<sup>3</sup> The structure was checked for possible higher symmetry using the ADDSYM algorithm from the program PLATON.<sup>4</sup> Crystal data and structure refinements are listed in Table S1. The atomic coordinates and equivalent isotropic displacement parameters are given in Table S2 in the Supporting Information (SI).

## Characterization

Powder XRD data of CKBFI were collected with a Bruker D2 PHASER diffractometer equipped with Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) at room temperature. A range of 2 $\vartheta$  values from 5 to 70 ° with a scan step width of 0.02 ° and a fixed counting time of 1 s.

Thermal gravimetric (TG) and differential scanning calorimetry (DSC) were measured on a simultaneous Netzsch STA 449C thermal analyzer instrument. Approximately 10 mg powder samples were placed in platinum crucibles and heated from room temperature to 700 °C at a rate of 5 °C min<sup>-1</sup> under a N<sub>2</sub> atmosphere.

The UV-Vis-NIR diffuse reflectance spectra of CKBFI were recorded by a Shimadzu SolidSpec-3700 DUV spectrophotometer in the wavelength range of 185-2600 nm. The IR spectra were collected with a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in the range of 400-4000 cm<sup>-1</sup>. Thin semi-transparent cylindrical plates for measurement were prepared by pressing a thoroughly ground mixture of about 5 mg powder sample of CKBFI and about 500 mg dried KBr (99.9 % purity).

Transmission measurement from 180 to 1600 nm was performed on a McPherson VUV as 2000 spectrophotometer by using an unpolished transparent crystal of approximately a 1 mm thickness.

Powder SHG testing was measured using a modified Kurtz-Perry method by a Q-switched Nd:  $YVO_4$  solid-state laser at 1064 nm, for visible and UV SHG. Polycrystalline CKBFI samples were ground and sieved into the following particle size ranges: 38 - 55, 55 - 88, 88 - 105, 105 - 150, 150 - 200, and 200 - 250  $\mu$ m, respectively. The

sieved KDP samples were used as references. The samples were pressed between two glass slides and secured in 1 mm thick aluminum holders with an 8 mm diameter hole.

## **Theoretical Calculation Details**

The first principles calculation for CKBFI was investigated using the plane wave Density Functional Theory (DFT) package CASTEP.<sup>5</sup> The exchange-correlation functional was treated by the generalized gradient approximation (GGA)<sup>6</sup> in the formulation of Perdew-Burke-Emzerhoff (PBE)<sup>7</sup> functional, and core-valence interactions were described by norm conserving pseudopotentials (NCPs). The cutoff energy of the plane wave was set to be 750 eV. Self-consistent field (SCF) calculations were performed with a convergence criterion of 1×10<sup>-5</sup> eV/atom on the total energy. The k-point grid was generated using the Monkhorst-Pack grid parameters as 4 × 4 × 2 for CKBFI, respectively. Pseudo atomic calculations are performed as follows: Cs 5s<sup>2</sup>5p<sup>6</sup>6s<sup>1</sup>, K 3s<sup>2</sup>3p<sup>6</sup>4s<sup>1</sup>, B 2s<sup>2</sup>2p<sup>1</sup>, O 2s<sup>2</sup>2p<sup>4</sup>, F 2s<sup>2</sup>2p<sup>5</sup>, I 5s<sup>2</sup>5p<sup>5</sup>. Because GGA usually underestimates the bandgap owing to the discontinuity of exchange-correlation energy, the HSE06 hybrid functional was chosen to provide more accurate band gap values. The linear optical properties (e.g., refractive index) were obtained using the real part of the dielectric function,  $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ . The NLO properties were calculated based on the length-gauge formalism derived by Aversa and Sipe.<sup>8</sup>

At a zero-frequency limit, the static SHG coefficients  $\chi^{(2)}_{\alpha\beta\gamma}$  can be attributed to Virtual-Electron (VE) and Virtual-Hole (VH) processes.<sup>9</sup> The SHG-weighted electron density analysis<sup>10</sup> was adopted to explore the origin of the NLO properties. The effective SHG contribution of each state (occupied and unoccupied) as weighting coefficient (after normalized with total VE or VH  $\chi^{(2)}_{\alpha\beta\gamma}$  value) are summed up to obtain the probability densities of all states. This method has been successfully applied in many previous studies.<sup>11</sup>

Empirical formula	CsKB <sub>8</sub> O <sub>12</sub> F <sub>2</sub> ·CsI	CsNH <sub>4</sub> B <sub>8</sub> O <sub>12</sub> F <sub>2</sub> ·CsI
Temperature (K)	293.15	293.15
Crystal system, space group	Trigonal, R32	Trigonal, R32
<i>a</i> / Å	6.5911(1)	6.60910(10)
<i>b</i> / Å	6.5911(1)	6.60910(10)
<i>c /</i> Å	30.6160(11)	30.8038(10)
γ /°	120	120
Volume /ų	1151.85(5)	1165.25(5)
Z , $ ho_{calc}$ /g·cm <sup>-3</sup>	3, 3.237	3, 3.109
μ /mm <sup>-1</sup>	7.107	6.760
F (000)	1006.669	984
artheta for data collection /°	2.00 to 27.46	1.983 to 27.435
Limiting indices	-8≤h≤8, -8≤k≤8, -39≤l≤39	-7≤h≤7, -8≤k≤8, -39≤l≤39
Reflections collected / unique	9704/604 [ <i>R</i> (int) = 0.0492]	9509/605 [ <i>R</i> (int) = 0.0592]
Completeness(%)	100.00	99.7
Data / restraints / parameters	604 / 0 / 43	605 / 12 / 41
Goodness-of-fit on F <sup>2</sup>	1.0448	1.100
Final <i>R</i> indices $[F_o^2 > 2\sigma(F_o^2)]^{[a]}$	$R_1 = 0.0186$ , w $R_2 = 0.0443$	$R_1 = 0.0287$ , w $R_2 = 0.0820$
<i>R</i> indices (all data) <sup>[a]</sup>	$R_1 = 0.0196$ , w $R_2 = 0.0449$	$R_1 = 0.0306$ , w $R_2 = 0.0831$
Largest diff. peak and hole/ $e \cdot Å^{-3}$	0.9029 and -0.7762	1.101 and -1.141
Flack parameter	-0.014(16)	0.016(18)

**Table S1**. Crystal data and structure refinement for CsKB<sub>8</sub>O<sub>12</sub>F<sub>2</sub>·CsI and CsNH<sub>4</sub>B<sub>8</sub>O<sub>12</sub>F<sub>2</sub>·CsI.

<sup>[a]</sup> $R_1 = \Sigma ||F_0| - |F||/\Sigma |F_0|$  and  $wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w F_0^4]^{1/2}$ 

			-	,		
Atoms	x	У	Z	U(eq)	BVS	
	CsKB <sub>8</sub> O <sub>12</sub> F <sub>2</sub> ·Csl					
Cs1	0	0	0.1238(11)	0.033(15)	0.72	
K1	0	0	0	0.023(3)	1.12	
B1	0.4033(7)	-0.0976(8)	0.0514(12)	0.0159(9)	3.07	
B2	2/3	1/3	0.0663(18)	0.0156(10)	3.11	
02	0.5680(5)	-0.1685(4)	0.0505(8)	0.016(6)	2.04	
01	0.4555(4)	0.1254(4)	0.0517(10)	0.022(6)	2.15	
F1	2/3	1/3	0.1125(11)	0.048(10)	0.87	
11	1/3	-1/3	1/6	0.034(16)	0.61	
	CsNH <sub>4</sub> B <sub>8</sub> O <sub>12</sub> F <sub>2</sub> ·CsI					
Cs(1)	1/3	2/3	0.5431(1)	0.034(1)	0.72	
B(1)	1/3	2/3	0.4011(3)	0.012(2)	3.13	
B(2)	0.7657(12)	0.9298(12)	0.3862(2)	0.013(1)	3.07	
O(1)	0.5411(7)	0.8765(7)	0.3865(2)	0.020(1)	1.95	
O(2)	0.8358(7)	0.7657(8)	0.3854(1)	0.013(1)	2.06	
F(1)	1/3	2/3	0.4469(2)	0.045(2)	0.71	
I(1)	1	1	5	0.036(1)	0.59	
N(1)	2/3	1/3	1/3	0.017(2)	/	

**Table S2**. Atomic coordinates, equivalent isotropic displacement parameters and bond valence sum (BVS) for CKBFI and CNBFI. U(eq) is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

Table S3. Selected bond lengths (	s (Å) and angles (	°) for CsKB <sub>8</sub> O <sub>12</sub> F <sub>2</sub> ·CsI
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Table S3. Selected bond lengths (Å) and angles (°) for CsKB <sub>8</sub> O <sub>12</sub> F <sub>2</sub> ·CsI.				
Cs1-01 <sup>#2</sup>	3.478(3)	B1-O2	1.380(5)	
Cs1-01	3.478(3)	B1-O2 <sup>#5</sup>	1.378(5)	
Cs1-O1 <sup>#1</sup>	3.478(3)	B1-O1	1.332(5)	
Cs1-O2 <sup>#3</sup>	3.350(3)	B2-O1	1.452(3)	
Cs1-O2 <sup>#4</sup>	3.350(3)	B2-O1 <sup>#4</sup>	1.452(3)	
Cs1-O2 <sup>#5</sup>	3.350(3)	B2-O1 <sup>#14</sup>	1.452(3)	
Cs1-F1 <sup>#6</sup>	2.971(3)	B2-F1	1.415(6)	
Cs1-I1	4.02507(12)			
Cs1-I1 <sup>#3</sup>	4.02507(12)	O1-B1-O2 <sup>#5</sup>	116.3(3)	
Cs1-I1 <sup>#7</sup>	4.02507(12)	O1-B1-O2	124.1(4)	
		O1 <sup>#14</sup> -B2-F1	107.9(2)	
K1-O1	3.117(2)	O1 <sup>#4</sup> -B2-F1	107.9(2)	
K1-O1 <sup>#11</sup>	3.117(2)	O1-B2-F1	107.9(2)	
K1-O1 <sup>#2</sup>	3.117(2)	O1 <sup>#14</sup> -B2-O1	111.0(2)	
K1-O1 <sup>#12</sup>	3.117(2)	O1 <sup>#4</sup> -B2-O1 <sup>#1</sup>	111.0(2)	
K1-O1 <sup>#13</sup>	3.117(2)	O1 <sup>#4</sup> -B2-O1	111.0(2)	
K1-O1 <sup>#1</sup>	3.117(2)			
K1-O2 <sup>#5</sup>	2.927(3)			
K1-O2 <sup>#3</sup>	2.927(3)			
K1-O2 <sup>#8</sup>	2.927(3)			
K1-O2 <sup>#9</sup>	2.927(3)			
K1-O2 <sup>#4</sup>	2.927(3)			
K1-O2 <sup>#10</sup>	2.927(3)			

Symmetry transformations used to generate equivalent atoms:

<sup>#1</sup>-Y,+X-Y,+Z; <sup>#2</sup>+Y-X,-X,+Z; <sup>#3</sup>-1+X,+Y,+Z; <sup>#4</sup>1+Y-X,1-X,+Z; <sup>#5</sup>-Y,-1+X-Y,+Z; <sup>#6</sup>-1/3-Y+X,1/3-Y,1/3-Z; <sup>#7</sup>+X,1+Y,+Z; <sup>#8</sup>-1-Y+X,-Y,-Z; <sup>#9</sup>+Y,-1+X,-Z; <sup>#10</sup>1-X,1-X+Y,-Z; <sup>#11</sup>-Y+X,-Y,-Z; <sup>#12</sup>+Y,+X,-Z; <sup>#13</sup>-X,-X+Y,-Z; <sup>#14</sup>1-Y,+X-Y,+Z

Cs1-O1 <sup>#3</sup>	3.465(3)	B2-O2 <sup>#10</sup>	1.378(6)
Cs1-O1 <sup>#2</sup>	3.465(3)	B2-O2	1.373(5)
Cs1-O1 <sup>#1</sup>	3.465(3)	B2-O1	1.339(6)
Cs1-O2 <sup>#4</sup>	3.330(3)	B1-F1	1.409(9)
Cs1-O2 <sup>#5</sup>	3.330(3)		
Cs1-O2 <sup>#6</sup>	3.330(3)	F(1)-B(1)-O(1)	108.0(5)
Cs1-F1	2.963(5)	F(1)-B(1)-O(1) <sup>#9</sup>	108.0(5)
Cs1-I1 <sup>#7</sup>	4.03988(17)	F(1)-B(1)-O(1) <sup>#8</sup>	108.0(5)
Cs1-I1 <sup>#1</sup>	4.03988(17)	O(1) <sup>#9</sup> -B(1)-O(1) <sup>#8</sup>	110.9(4)
Cs1-I1 <sup>#4</sup>	4.03988(17)	O(1) <sup>#9</sup> -B(1)-O(1)	110.9(4)
		O(1)-B(1)-O(1) <sup>#8</sup>	110.9(4)
B1-O1 <sup>#8</sup>	1.453(4)	O(1)-B(2)-O(2) <sup>#10</sup>	116.2(5)
B1-O1	1.453(4)	O(1)-B(2)-O(2)	123.8(6)
B1-O1 <sup>#9</sup>	1.453(4)		

Table S4. Selected bond lengths (Å) and angles (°) for  $CsNH_4B_8O_{12}F_2\cdot CsI.$ 

Symmetry transformations used to generate equivalent atoms:

<sup>#1</sup>1-Y+X,2-Y,1-Z; <sup>#2</sup>-1+Y,+X,1-Z; <sup>#3</sup>1-X,-X+Y,1-Z; <sup>#4</sup>-Y+X,1-Y,1-Z; <sup>#5</sup>+Y,+X,1-Z; <sup>#6</sup>1-X,1-X+Y,1-Z; <sup>#7</sup>-Y+X,2-Y,1-Z; <sup>#8</sup>+Y-X,1-X+Y,1-Z; <sup>#6</sup>+Y,1-Z; <sup>#6</sup>+Y

X,+Z; <sup>#9</sup>1-Y,1+X-Y,+Z; <sup>#10</sup>1+Y-X,2-X,+Z

atoms	x	У	Z	U(eq)
H1a	0.7549	0.2797	0.3446	0.021
H1b	0.6805	0.3688	0.3052	0.021
H1c	0.5173	0.2349	0.3396	0.021
H1d	0.7549	0.3797	0.3446	0.021
Table S6. Hydrogen bonds for CsNH4B8F12. Csl. D, donor; H, hydrogen; A, acceptor.				
D-H···A	d <sub>(D-H)</sub> /Å	d <sub>(H-A)</sub> /Å	d <sub>(D-A)</sub> /Å	D-H-A/°
N1-H1a…O2 <sup>#2</sup>	0.89	2.10(3)	2.97 (3)	165.9(9)
N1-H1c…O2 <sup>#1</sup>	0.89	2.16(3)	2.97(3)	151.3(8)
N1-H1d…O2	0.89	2.10(3)	2.97(3)	164.3(8)

Table S5. Hydrogen coordinates (Å) and isotropic displacement parameters (Å<sup>2</sup>) for CsNH<sub>4</sub>B<sub>8</sub>F<sub>12</sub>·CsI.

<sup>#1</sup>1-Y, +X-Y, +Z; <sup>#2</sup>1+Y-X, 1-X, +Z



Figure S1. (a) The torsion angle of  $[B_3O_6]^{3\text{-}}$  and (b) the 18-MRs in  $\text{CsKB}_8\text{O}_{12}\text{F}_2.$ 



**Figure S2**. Comparison of the flatness value with the <sup>2</sup><sub>∞</sub>[B<sub>4</sub>O<sub>6</sub>F] layers. (a)(b) The angles of two [B<sub>3</sub>O<sub>7</sub>F]<sup>6-</sup> of NH<sub>4</sub>B<sub>4</sub>O<sub>6</sub>F, and RbB<sub>4</sub>O<sub>6</sub>F; (c)(d) The angles between two [B<sub>3</sub>O<sub>6</sub>]<sup>3-</sup> of CsB<sub>4</sub>O<sub>6</sub>F ,CsKB<sub>8</sub>O<sub>12</sub>F<sub>2</sub> and CsKB<sub>8</sub>O<sub>12</sub>F<sub>2</sub>·CsI (this work).



Figure S3. Comparison of the position of F. (a) The F atom is embedded in the 6-MRs ring, such as (b) NaB<sub>4</sub>O<sub>6</sub>F, (c) RbB<sub>4</sub>O<sub>6</sub>F and (d) NH<sub>4</sub>B<sub>4</sub>O<sub>6</sub>F; (e) The F atom locates outside in the 6-MRs ring, such as (f) CsB<sub>4</sub>O<sub>6</sub>F, (g) CsKB<sub>8</sub>O<sub>12</sub>F<sub>2</sub>, (h) CsRbB<sub>8</sub>O<sub>12</sub>F<sub>2</sub>, (i) CsAB<sub>8</sub>O<sub>12</sub>F<sub>2</sub>·CsI(A=K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>).



Figure S4. Experimental and calculated PXRD patterns of CKBFI.



Figure S5. TG-DSC curves of CKBFI, only one evident endothermic peak at 542  $^{\circ}\mathrm{C}$  for CKBFI.



Figure S6. The experimental (calcined at different temperatures) PXRD patterns of CKBFI.



Figure S7. IR spectrum for CKBFI.



Figure S8. Band structure of CKBFI.

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