# Electronic Supplementary Information (ESI) for

# CsAlB<sub>3</sub>O<sub>6</sub>F: A Beryllium-Free Deep-Ultraviolet Nonlinear Optical Material with Enhanced Thermal Stability

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#### **Experimental Procedures**

**Reagents.** Cesium fluoride (CsF, 99%), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>, 99.99%), ammonium hexafluoroaluminate ((NH<sub>4</sub>)<sub>3</sub>AlF<sub>6</sub>, 99%), and boric acid (H<sub>3</sub>BO<sub>3</sub>, 99%) were obtained from Aladdin Chemical Industry Co., Ltd. All chemicals were used as received.

**Synthesis.** Single crystals of the title compound were obtained by spontaneous crystallization from high temperature solution. The mixture of CsF,  $(NH_4)_3AIF_6$ , and  $H_3BO_3$  (with a molar ratio of 2:1:3) was thoroughly ground and melt at 700 °C, and then cooled slowly down to 500 °C at a rate of 2 °C h<sup>-1</sup> before turning off the furnace. The sub-millimeter-sized crystals were separated mechanically from the crucible. Polycrystalline samples of CABF were synthesized *via* standard solid-state reaction. Stoichiometric mixtures of CsF,  $AI_2O_3$  and  $H_3BO_3$  were mixed thoroughly and loaded into a corundum crucible. The samples were sintered at 500 °C for 3 d with several intermittent regrindings. The sample purity was confirmed by the powder X-ray diffraction (PXRD) study (see Figure S4).

**Single-Crystal X-ray Diffraction.** Single crystal XRD data were recorded on a SMART APEX II diffractometer (Bruker Corporation, Germany) using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data integration and absorption corrections were carried out using the *SAINT*<sup>1</sup> program. The single crystal data were analyzed with the *Olex2* program<sup>2</sup>. The structure was solved using Intrinsic Phasing method<sup>3</sup>, and refined using the least–squares technique on  $F_0^2$  with data having  $F_0^2 \ge 2\sigma$  ( $F_0^2$ ). To verify the absence or presence of the F atoms, elemental analysis was performed (Figure S5). The structure was checked for possible higher symmetry using the *ADDSYM* algorithm from the program *PLATON*.<sup>4</sup> Crystal data and structure refinement information are given in Table S1. The final refined atomic positions and isotropic thermal parameters are summarized in Table S2. Selected bond distances and angles are listed in Table S3.

**PXRD**. PXRD data were collected at room temperature with a D8 advance X-ray diffractometer (Bruker Corporation, Germany), operating at 40 kV and 40 mA with Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å). Data were collected in the angular (2 $\vartheta$ ) range of 10–70° with a scan step width of 0.02° and a fixed counting time of 2 s. Rietveld refinement of the structural model was performed by GSAS-II software<sup>5</sup>.

**Scanning Electronic Microscope (SEM) images and Energy Dispersive X-Ray (EDX) microanalysis.** SEM images and EDX microanalysis of the samples were obtained from a XL-30 environmental scanning electron microscope (Philips Corporation, Netherlands) operating at an acceleration voltage of 10 kV.

**Thermal Analysis.** Thermal gravimetric (TG) analysis and differential scanning calorimetry (DSC) were measured on a simultaneous STA 449 F3 thermal analyzer (NETZSCH Corporation, Germany) in a flowing N<sub>2</sub> atmosphere, heated from room temperature to 900 °C at a rate of 10 °C min<sup>-1</sup>.

**Infrared Spectroscopy.** The Infrared spectrum was recorded with an IR Affinity-1 Fourier transform infrared spectrometer (Shimadzu Corporation, Japan) in the range of 400 - 4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. Pellets for measurement were prepared by pressing a thoroughly ground mixture of 5 mg sample and 500 mg dried KBr.

**UV–Vis–NIR Diffuse Reflectance Spectroscopy.** The diffuse reflectance spectrum was measured at room temperature with a SolidSpec-3700DUV spectrophotometer (Shimadzu Corporation, Japan) in the 190–1100 nm wavelength range. The reflectance spectra were converted to absorbance using the e Kubelka–Munk relation.

**Second-Order NLO Measurements.** The powder SHG responses of CABF were measured by the Kurtz–Perry method<sup>6</sup> with a Q-switched Nd: YAG solid-state laser at 1064/532 nm. Polycrystalline samples were ground and sieved into the following particle size ranges: 38–55, 55–88, 88–105, 105–155, 155–200, and 200–250  $\mu$ m. The sieved KDP and BBO samples with the same particle ranges were used as a reference. No index-matching oil was used.

**Computational Methods.** The first-principles calculations for CABF were performed by using CASTEP<sup>7</sup> package. The norm-conserving pseudopotentials (NCP)<sup>8, 9</sup> and Perdew-Burke-Emzerhoff

(PBE) functional within the generalized gradient approximation (GGA) were adopted.<sup>10</sup> The plane-wave energy cutoff and Monkhorst-Pack k-point in the Brillouin zone were set at 850.0 eV and  $3 \times 2 \times 4$ , respectively. In order to guarantee the accuracy of optical properties, the empty bands were set as three times of valence bands. Because GGA usually underestimates the bandgap owing to the discontinuity of exchange-correlation energy,<sup>11, 12</sup> the HSEO6 hybrid functional was chosen to provide more accurate band gap values.<sup>12, 13</sup> Based on the scissorcorrected (1.55 eV) electron structure, the linear optical properties (e.g., refractive index) were obtained by the Kramers-Kronig transform. The NLO properties were calculated based on the length-gauge formalism.<sup>14</sup> At a zero-frequency limit, the static SHG coefficients  $x_{abr}^{(2)}$  can be attributed to Virtual-Electron (VE) and Virtual-Hole (VH) processes.<sup>15</sup> To investigate the origin of the NLO properties, the SHG-weighted electron density analysis<sup>16</sup> was adopted. The effective SHG contributions of each state (occupied and unoccupied) as weighting coefficient (after normalized with total VE or VH  $x_{aby}^{(2)}$  value) sum up to obtain the probability densities of all states. This method has been successfully applied in many previous studies.<sup>17, 18</sup> In addition, the binding energy of title compounds is defined as the total energy of crystal cell subtracting the sum of energy of the  $(AIB_3O_6F)_{\infty}$  layers and isolated Cs cations.

# **Results and Discussion**

formula	CsAIB <sub>3</sub> O <sub>6</sub> F (CABF)
fw	307.32
crystal system	Orthorhombic
space group	<i>Pna</i> 2 <sub>1</sub> (No. 33)
<i>a</i> (Å)	8.064(3)
<i>b</i> (Å)	11.970(4)
<i>c</i> (Å)	7.036(3)
V (ų)	679.2(4)
Ζ	4
ρ <sub>calcd</sub> (g⋅cm <sup>-3</sup> )	3.005
$\mu$ (mm <sup>-1</sup> )	5.580
F(000)	560
crystal size (mm)	$0.198 \times 0.136 \times 0.126$
R <sub>int</sub>	0.0463
completeness	100.0 %
GOF (F <sup>2</sup> )	1.022
final <i>R</i> indices [I>2 $\sigma$ (I)] <sup>[a]</sup>	$R_1 = 0.0283, wR_2 = 0.0567$
R indices (all data) <sup>[a]</sup>	$R_1 = 0.0502, wR_2 = 0.0643$
Flack factor	-0.04(6)
largest diff. peak and hole (e·Å <sup>-3</sup> )	0.724 and -0.755

**Table S1.** Crystal data and structure refinement for  $CsAlB_3O_6F$ .

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

Atom	Wyck.	x/a	y/b	z/c	$U_{\rm eq}^{[a]}$	BVS <sup>[b]</sup>
Cs(1)	4 <i>a</i>	0.4939(1)	0.7280(1)	0.1395(3)	0.034(1)	0.83
Al(1)	4 <i>a</i>	0.2799(2)	0.4240(2)	0.1288(5)	0.022(1)	3.14
B(1)	4 <i>a</i>	0.1909(15)	0.5548(9)	0.4486(14)	0.026(2)	2.99
B(2)	4 <i>a</i>	0.2126(16)	0.6922(10)	0.6898(13)	0.030(3)	3.10
B(3)	4 <i>a</i>	0.1887(13)	0.4994(8)	0.7737(14)	0.022(2)	3.01
O(1)	4 <i>a</i>	0.1977(8)	0.5311(5)	0.2617(7)	0.028(1)	2.02
O(2)	4 <i>a</i>	0.1976(8)	0.6668(5)	0.5031(8)	0.025(1)	2.12
O(3)	4 <i>a</i>	0.2360(9)	0.7984(5)	0.7491(9)	0.039(2)	1.98
O(4)	4 <i>a</i>	0.2042(9)	0.6108(5)	0.8269(8)	0.027(1)	2.07
O(5)	4 <i>a</i>	0.1766(7)	0.4725(4)	0.5840(7)	0.021(1)	2.08
O(6)	4 <i>a</i>	0.1931(7)	0.4173(5)	0.9036(8)	0.027(1)	2.02
F(1)	4 <i>a</i>	0.4804(6)	0.4545(6)	0.0941(11)	0.064(2)	0.78

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for CsAlB<sub>3</sub>O<sub>6</sub>F.

<sup>[a]</sup>  $U_{eq}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor. <sup>[b]</sup> Bond valence sums are calculated by using bond-valence theory<sup>19</sup> (S<sub>i</sub> = exp[( $R_o - R_i/B$ ], where  $R_o$  is an empirical constant,  $R_i$  is the length of bond *I* (in angstroms), and B= 0.37).

Cs(1)-O(1)#1	3.428(6)	O(1)-Al(1)-O(3)#6	110.7(3)
Cs(1)-O(1)	3.464(6)	O(1)-AI(1)-O(6) <sup>#3</sup>	112.1(3)
Cs(1)-O(2)#1	3.291(6)	O(3)#6-Al(1)-O(6) <sup>#3</sup>	112.2(3)
Cs(1)-O(2)	3.577(6)	F(1)-AI(1)-O(1)	106.8(4)
Cs(1)-O(3)#2	3.385(7)	F(1)-AI(1)-O(3) <sup>#6</sup>	109.4(4)
Cs(1)-O(3) <sup>#3</sup>	3.546(7)	F(1)-AI(1)-O(6) <sup>#3</sup>	105.5(4)
Cs(1)-O(4) <sup>#2</sup>	3.382(6)	O(1)-B(1)-O(2)	118.0(8)
Cs(1)-O(4)#3	3.502(6)	O(1)-B(1)-O(5)	121.9(8)
Cs(1)-O(5)#4	3.256(5)	O(5)-B(1)-O(2)	120.1(8)
Cs(1)-O(6)#4	3.296(6)	O(2)-B(2)-O(4)	121.2(9)
Cs(1)-O(6) <sup>#5</sup>	3.585(6)	O(3)-B(2)-O(2)	121.6(9)
Cs(1)-F(1)	3.292(7)	O(3)-B(2)-O(4)	117.2(7)
Al(1)-O(1)	1.719(6)	O(5)-B(3)-O(4)	119.4(8)
AI(1)-O(3) <sup>#6</sup>	1.730(7)	O(6)-B(3)-O(4)	121.1(8)
Al(1)-O(6) <sup>#3</sup>	1.734(6)	O(6)-B(3)-O(5)	119.4(8)
Al(1)-F(1)	1.675(5)		
B(1)-O(1)	1.347(11)		
B(1)-O(2)	1.395(11)		
B(1)-O(5)	1.375(11)		
B(2)-O(2)	1.354(12)		
B(2)-O(3)	1.352(14)		
B(2)-O(4)	1.373(12)		
B(3)-O(4)	1.391(11)		
B(3)-O(5)	1.377(12)		
B(3)-O(6)	1.342(10)		

Table S3. Selected bond distances and angles (Å) of CsAlB<sub>3</sub>O<sub>6</sub>F.

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+3/2,z; #2 x+1/2,-y+3/2,z-1; #3 x,y,z-1; #4 -x+1/2,y+1/2,z-1/2; #5 -x+1,-y+1,z-1/2; #6 - x+1/2,y-1/2,z-1/2; #7 x-1/2,-y+3/2,z; #8 x-1/2,-y+3/2,z+1; #9 x,y,z+1; #10 -x+1/2,y-1/2,z+1/2; #11 -x+1,-y+1,z+1/2; #12 -x+1/2,y+1/2,z+1/2

	Cutoff edge (nm)	PSHG (×KDP)	Birefringence (calc.)	Shortest matching (nm) <sup>a</sup>	phase- wavelength	Decomposition/meltin g temperature (°C)	Crystal growth condition
KBBF <sup>20</sup>	149 (calc. PBEO) 147 (exp.)	1.2	0.062@546 nm	161 (exp.)		820	Open system, layered habit and Toxic BeO
$Li_2B_6O_9F_2^{21}$	154 (calc. HSE06) 156 (exp.)	1.3	0.070@1064 nm	192 (calc.)		518	Closed system
$NH_4B_4O_6F^{22}$	158 (calc. HSE06) 156 (exp.)	3.0	0.107@1064 nm	164 (calc.) 158 (exp.)		~300	Closed system
$CsB_4O_6F^{23}$	155 (calc. HSE06) 155 (exp.)	1.9	0.098@1064 nm	175 (calc.) 172 (exp.)		609	Open system
$RbB_4O_6F^{24}$	160 (cal. HSE06) <200 (exp.)	0.8	0.102@1064 nm	165 (calc.)		452	Open system
$CsKB_8O_{12}F_2^{24}$	160 (calc. HSE06) <200 (exp.)	1.9	0.105@1064 nm	170 (calc.)		412	Open system
$CsRbB_8O_{12}F_2^{24}$	<200 (exp.)	1.1	N/A	N/A		582	Open system
$NaB_4O_6F^{25}$	164 (calc. HSE06) <200 (exp.)	0.9	0.120@1064 nm	166 (calc.)		~400	Closed system
$CaB_{5}O_{7}F_{3}{}^{26}$	141 (calc. PBEO) <180 (exp.)	2.3	0.072@546 nm	171 (calc.)		~630	Closed system
$SrB_5O_7F_3^{26}$	143 (calc. PBE0) <200 (exp.)	2.5	0.077@546 nm	169 (calc.)		~630	Closed system
$NaNH_4PO_3F \cdot H_2O^{27}$	<176 (exp.)	1.1	> 0.053@589.3 nm	194 (calc.)		100	Aqueous system

## Table S4. Comparison of basic properties of KBBF and recently reported potential UV and DUV NLO crystals.

Aluminum borates or aluminum borate fluorides

$K_2AI_2B_2O_7^{28}$	180 (exp.)	1.0	0.07@1064 nm	233 (exp.)	1052	Open system
BaAIBO <sub>3</sub> F <sub>2</sub> <sup>29, 30</sup>	165 (exp.)	3.2	0.042@1064 nm	273 (exp.)	974	Open system
YAI <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> <sup>31, 32</sup>	170 (exp.)	N/A	0.070@1064 nm	246 (exp.)	1280	Open system
$\theta$ -Rb <sub>2</sub> Al <sub>2</sub> B <sub>2</sub> O <sub>7</sub> <sup>33</sup>	<200	2.0	0.057@1064 nm	N/A	600	Open system
$K_3Ba_3Li_2AI_4B_6O_{20}F^{34, 35}$	~190	1.5	0.052@532 nm	243 (exp.)	874	Open system
$Rb_3Ba_3Li_2Al_4B_6O_{20}F^{36}$	198	1.5	0.057 @1064 nm	243 (exp.)	856	Open system
$Rb_{3}Al_{3}B_{3}O_{10}F^{37}$	~200	1.2	N/A	N/A	1189	Open system
$Cs_2Al_2(B_3O_6)_2O^{38}$	<185 (exp.) 176 (calc. HSE06)	~0.5	0.136 @ 177.3 nm	N/A	800	Open system
CsAlB <sub>3</sub> O <sub>6</sub> F <sup>*</sup>	166 (calc. HSE06) <190 (exp.)	2.0	0.091 @1064 nm	182 (calc.)	704	Open system

N/A = Not available; <sup>*a*</sup> For practical DUV application, the shortest phase-matching wavelength must be below 200 nm; <sup>\*</sup>This work.



**Figure S1.** The comparison of  $[BO_xF_{4-x}]$  (x = 1, 2, 3), BeO<sub>3</sub>F and  $[AIO_mF_n]$  (m + n = 4, 5, 6, AIOF) structural units. Experimental structural data were obtained from the Inorganic Crystal Structure Database (ICSD).



**Figure S2.** The coordination environment of the Cs<sup>+</sup> cation in CABF. (a) The [CsO<sub>11</sub>F] polyhedron. (b) The cationic chain. (c) The crystal structure of CABF viewing along the a axis.



**Figure S3.** The IR spectrum of CABF. The strong absorption bands at 1400 and 1304 cm<sup>-1</sup> are assigned to the asymmetric stretching of the  $[BO_3]$  groups; The peaks near 1062 and 1014 cm<sup>-1</sup> attribute to symmetric stretching of the  $[BO_3]$  groups. The peak at 851 cm<sup>-1</sup> could be attributed to the out-of-plane bending of the  $[BO_3]$  groups, and the peaks at 714 and 466 cm<sup>-1</sup> could arise from the stretching-bending vibrations of the  $[AIO_3F]$  units.



**Figure S4.** Experimental (red circles) and calculated (blue line) PXRD patterns and their difference (black line) for the PXRD Rietveld refinement of CABF. The short vertical lines show the positions of Bragg reflections of the calculated pattern; impurity is not observed. The refined unit cell parameters are a = 8.062 Å, b = 11.969 Å, c = 7.035 Å, and V = 678.893 Å<sup>3</sup>, which are close to the parameters obtained from single crystal data.



**Figure S5.** EDX spectroscopy and SEM image (inset) of CABF. The EDX analysis indicates that the molar ratio of O: F is 48.87: 7.65, which is approximately equal to the theoretical molar ratio of 6 : 1, further verifying the existence of fluorine in the crystal structure.



**Figure S6.** (a) The PXRD patterns of CABF before and after melting. The PXRD pattern after melting of CABF is very close to the original one except two peaks at 22.1 and 26.9° (those peaks are later assigned to  $Cs_2Al_2(B_3O_6)_2O^{38}$ ). To explain the observed  $Cs_2Al_2(B_3O_6)_2O$  impurity, we speculate that the following reaction mechanism:  $2CsAlB_3O_6F + H_2O \Rightarrow Cs_2Al_2(B_3O_6)_2O + 2HF$ , where the adsorbed water comes from the air. In addition, the  $Cs_2Al_2(B_3O_6)_2O$  impurity can be removed if the sample is mixed with a certain amount of  $NH_4F$  (decompose to HF and  $NH_3$  on heating) and calcined at 600 °C for 8 h, which reveals that aforementioned reaction is reversible. (b) High-temperature in *situ* PXRD patterns of CABF at different temperature (inset: enlarged area from 22 to 29°). It is shown that the room-temperature CABF phase changes to an unknown phase (index failed) above 480 °C, which indicates a phase transition or temperature-mediated polymorphism of CABF. However, after several attempts, only room-temperature CABF phase (denoted as  $\alpha$ -CABF) can be identified after cooling from high temperature. We will further discuss this matter in a separate contribution. Thus, single crystals of CABF were grown by high temperature solution method with excessive amount of fluorides as the flux.



**Figure S7.** PSHG measurements at 532 nm. The inset shows that the SHG intensity of CABF is ~1/6 times that of BBO (particle size range: 200–250  $\mu$ m) at 532 nm fundamental wave laser radiation.



**Figure S8.** The arrangement of the planar  $B_3O_6$  groups in CBF (left) and CABF (right). For convenience, the center of  $B_3O_6$  groups in each compound was shifted manually to the same point. The rotational angle ( $\vartheta$ ) describes the separation of  $B_3O_6$  groups caused by rotation among different borate layers, while the deviation angle ( $\varphi$ ) stands for the angle between the  $B_3O_6$  plane and the lattice plane within the same borate layer. To maximum the macro SHG performance, both  $\vartheta$  and  $\varphi$  should be as small as possible.



Figure S9. The calculated (a) bandgap and (b) PDOS of CABF.



Figure S10. The calculated refractive index of CABF.



Figure S11. SHG density maps of the occupied and unoccupied orbitals in the VH process of CABF.

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