Electronic Supplementary Information

$A_2B_6O_9F_2$ (A = NH$_4$, K): New members of $A_2B_6O_9F_2$ family with deep-UV cutoff edge and moderate birefringence

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EXPERIMENTAL SECTION

Single-Crystal Growth

Single-crystal of $(NH_4)_2B_6O_9F_2$ was grown with NH_4F as the flux in a sealed system by a high-temperature solution method. NH_4F (Aladdin, 98 %) and B_2O_3 (Aladdin, 98 %) were evenly mixed in a molar ratio of 2:1 into a sealed platinum crucible. The platinum crucible was heated from room temperature to 300 °C for 10 h, then held at this temperature for 1 day, and finally cooled first to 240 °C at a rate of 1.5 °C·h^{-1} and then to room temperature quickly. Colorless crystal of $(NH_4)_2B_6O_9F_2$ with the largest size of $2 \times 3 \times 1$ mm^3 was obtained from the product with yields of about 60 % - based on B. Polycrystalline samples of $(NH_4)_2B_6O_9F_2$ were prepared by grinding single crystals.

Single crystals of $K_2B_6O_9F_2$ were obtained by the high-temperature solution method in the sealed silica tube. The mixture of KBF_4 (Aladdin, 99%), KNO_3 (Aladdin, 99 %), $Li_2B_4O_7$ (Aladdin, 99 %) and $LiBO_2$ (Aladdin, 99.9 %) with a molar ratio of 1:1:1:1 was put into a silica tube, sealed under 10^{-3} Pa, and heated at 400 °C for 2 days, then cooled to 50 °C at a rate of 1 °C·h^{-1}. Millimeter-sized crystals were selected from the products for single crystal data testing. However, polycrystalline samples of $K_2B_6O_9F_2$ were not obtained due to the low yield of the crystals.

Powder X-ray Diffraction (XRD)

Powder XRD data were collected using the Bruker D2 PHASER X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) in the range of 10 - 70 ° (2θ) with a fixed counting time and a scan step width of 0.02 °and a fixed counting time of 1s per step.

Single-Crystal XRD

XRD data for single $(NH_4)_2B_6O_9F_2$ and $K_2B_6O_9F_2$ crystals with good quality and appropriate size were collected using the Bruker SMART APEX II 4K CCD diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) at 273.15 K and Mo Kα radiation ($\lambda = 0.71073$ Å) at 300 K, respectively. Then, the diffraction data were restored and corrected by the SAINT and SCALE programs, respectively. [1] The structure data were analyzed and refined by SHELXTL,[2] and the direct method was used for structure analysis. The correctness of the structures was checked by the PLATON program[3] and the international crystal society online testing website (http://checkcif.iucr.org/).

Energy Dispersive X-ray Spectroscope (EDS)

Elemental analysis was carried on a clean single crystal surface by means of a field emission scanning electron microscope (SEM, SUPRA 55VP) with an Oxford X-MasN energy dispersive X-ray (EDS) detector.

Infrared (IR) Spectroscopy

The coordination environment of B atoms was determined by recording the IR spectrum on a Shimadzu IRAffinity-1 Fourier transform IR spectrometer in the range of 400 - 4000 cm^{-1}.

UV-Vis NIR Transmittance Spectroscopy

The UV-Vis NIR transmittance spectrum was measured on a crystal plate without any polishing in the range of 180 - 1600 nm at room temperature with a Shimadzu SolidSpec-3700DUV

spectrophotometer to determine the cutoff edge of the $(NH_4)_2B_6O_9F_2$ crystal.

TG-DSC Analysis

The thermal behavior of $(NH_4)_2B_6O_9F_2$ was analyzed by a NETZSCH STA 449C simultaneous analyzer from 40 to 700 °C with a heating rate of 10 °C·min^{-1} under flowing nitrogen gas.

Water Dissolution Test

The dissolution of selected millimeter-sized transparent crystals was tested at 24 °C (room temperature) and atmospheric pressure using water as solvent. An excess of $(NH_4)_2B_6O_9F_2$ crystals was dissolved in 100 mL of water, and stirred for 48 h to reach equilibrium. The undissolved crystals were then dried and weighed.

Computational Details

The electronic structures, optical properties, and density of states (DOS) of $A_2B_6O_9F_2$ (A = NH_4^+, K^+) were calculated by the density functional theory in the CASTEP package.[4] The interactions between ionic cores and electrons were described by the norm-conserving pseudopotential. The exchange-correlation functionals were the Perdew-Burke-Ernzerhof (PBE) functionals within the generalized gradient approximation (GGA).[5,6] The plane-wave energy cutoff was set at 780.0 eV for both compounds, and the separation of k-point was set as 0.03 Å for $(NH_4)_2B_6O_9F_2$, and 0.02 Å for $K_2B_6O_9F_2$ in the Brillouin zone.[7] The H-$1s^1$, B-$2s^22p^1$, N-$2s^22p^3$, O-$2s^22p^4$ and F-$2s^22p^5$ orbital electrons for $(NH_4)_2B_6O_9F_2$ and B-$2s^22p^1$, O-$2s^22p^4$, F-$2s^22p^5$ and K-$3s^23p^64s^1$ for $K_2B_6O_9F_2$ were treated as valence electrons. During the optical property calculations, the number of empty bands was set to three times that of valence bands to ensure the convergence of refractive indices. It is well known that GGA-PBE usually underestimates the band gap because of its limitation, so the Heyd-Scuseria-Ernzerhof (HSE06) functional[8] was used to obtain more accurate band gaps and scissor operators of 1.21 eV for $(NH_4)_2B_6O_9F_2$ and 1.60 eV for $K_2B_6O_9F_2$ were applied to move the simulated conduction bands to the right place.

The linear optical refractive indices were calculated by using the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$.[6] The imaginary part of $\varepsilon_2(\omega)$ was obtained from the equation:

$$\varepsilon_2\left(q\rightarrow O_{\hat{u}}, h\omega\right) = \frac{2e^2\pi}{\Omega\varepsilon_o} \sum_{kcv} \left|\langle\varphi_k^c|u\cdot r|\varphi_k^v\rangle\right|^2 \delta\left[E_k^c - E_k^v - E\right]$$

where e is the elementary charge, h is Planck's constant, r is the position operator, u is the vector defining the polarization of the incident, Ω is the volume of the unit cell, ε_o is the dielectric constant, φ_k^v and φ_k^c denote the momentum matrix element transition. E_k^c and E_k^v are energies of the occupied and empty electronic states, respectively. Then, the birefringence Δn was determined by the real part of the dielectric function $\varepsilon_1(\omega)$ via the Kramers-Kronig transformation.[9]

Table 1 Crystal data and structure refinement for $(NH_4)_2B_6O_9F_2$ and $K_2B_6O_9F_2$.

Empirical formula	$(NH_4)_2B_6O_9F_2$	$K_2B_6O_9F_2$
Formula weight	282.94	325.06
Temperature / K	273.15	300.00
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pbca$
a / Å	6.1553(9)	11.7129(10)
b / Å	12.1758(19)	10.3030(7)
c / Å	14.5192(17)	15.4140(11)
β / °	113.443 (6)	90
Volume / Å^3	998.3(3)	1860.1(2)
Z	4	8
ρ_{calc} / g·cm^{-3}	1.883	2.321
μ / mm^{-1}	1.736	1.090
$F(000)$	568.0	1264.0
Radiation	Cu Kα (λ = 1.54178)	Mo Kα (λ = 0.71073)
2θ range for data collection / °	9.84 to 136.64	5.28 to 54.96
Index ranges	$-7 \leq h \leq 7$, $-11 \leq k \leq 14$, $-16 \leq l \leq 17$	$-15 \leq h \leq 15$, $-11 \leq k \leq 13$, $-20 \leq l \leq 19$
Reflections collected	6324	15107
Independent reflections	1803 [R_{int} = 0.0394, R_{sigma} = 0.0385]	2134 [R_{int} = 0.0780, R_{signa} = 0.0473]
Data / restraints / parameters	1803 / 0 / 172	2134 / 0 / 172
Goodness of fit on F^2	1.085	1.076
Final R indexes [$I \geq 2\sigma (I)$][a]	R_1 = 0.0382, wR_2 = 0.1020	R_1 = 0.0371, wR_2 = 0.0760
Final R indexes [all data][a]	R_1 = 0.0450, wR_2 = 0.1073	R_1 = 0.0558, wR_2 = 0.0891
Largest diff. peak / hole / e·Å^{-3}	0.21 / $-$ 0.27	0.29 / $-$ 0.41

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma wF_o{}^4]^{1/2}$

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) and the bond valence sum (BVS) for each atom in the asymmetric unit for $(NH_4)_2B_6O_9F_2$ and $K_2B_6O_9F_2$.

Atoms	x	y	z	U_{eq}[a]	BVS[b]
		$(NH_4)_2B_6O_9F_2$			
B1	− 2603(4)	− 793(2)	− 3070.0(17)	23.9(5)	3.0
B2	886(4)	− 768(2)	− 1470.5(17)	24.1(5)	3.0
B3	692(4)	− 1941.9(19)	− 2877.7(17)	24.3(5)	3.0
B4	3627(4)	− 3299(2)	− 2891.6(18)	25.2(5)	3.0
B5	− 6028(4)	516.5(19)	− 3497.3(16)	23.2(5)	3.0
B6	3481(4)	540(2)	− 1900.9(17)	25.2(5)	3.0
N1	2256(3)	− 3491.5(18)	− 387.5(15)	38.3(5)	
N2	6821(3)	− 1720.9(17)	− 259.9(14)	35.6(5)	
O1	− 4764(2)	− 407.3(12)	− 3701.2(10)	27.6(4)	1.8
O2	− 1514(2)	− 450.8(13)	− 2113.0(10)	29.1(4)	1.9
O3	− 1566(2)	− 1574.6(12)	− 3468.4(10)	28.3(4)	1.9
O4	1751(2)	− 1687.0(12)	− 1894.3(10)	25.6(3)	1.8
O5	1718(3)	− 2608.5(13)	− 3353.7(11)	32.1(4)	2.0
O6	4419(2)	− 3554.3(12)	− 1909.3(10)	25.9(3)	1.8
O7	4726(3)	− 3681.8(13)	− 3492.0(10)	31.4(4)	1.9
O8	− 7262(2)	211.5(13)	− 2866.6(10)	28.5(4)	1.9
O9	2558(2)	152.5(12)	− 1253.2(10)	27.9(4)	1.8
F1	910(2)	− 1124.5(12)	− 529.1(9)	37.4(3)	0.7
F2	− 7749(2)	838.5(10)	− 4452.6(8)	30.8(3)	0.7
		$K_2B_6O_9F_2$			
K1	4318.9(6)	2609.5(6)	4096.6(5)	33.89(19)	1.1
K2	5719.1(6)	6322.8(6)	3531.9(4)	31.23(18)	1.0
B1	6747(3)	3941(3)	5143(2)	19.5(6)	3.1
B2	8401(3)	4246(3)	4161.6(19)	18.2(6)	3.1
B3	10222(3)	4512(3)	3352(2)	19.9(6)	3.0
B4	8558(3)	5985(3)	3147(2)	19.6(6)	3.1
B5	8332(3)	8086(3)	2305(2)	20.6(6)	3.1
B6	7733(3)	9609(3)	1232(2)	22.8(6	3.1
O1	7788.8(15)	3545.5(16)	4731.9(11)	19.0(4)	2.1
O2	9462.8(16)	3854.4(17)	3951.8(12)	22.2(4)	2.1
O3	7931.6(16)	5337.1(18)	3760.7(13)	25.2(4)	2.1
O4	9618.8(16)	5619.6(17)	2923.1(13)	23.0(4)	2.1
O5	8001.4(16)	7023.9(18)	2786.2(13)	25.8(5)	2.1
O6	9404.3(16)	8564.2(17)	2313.6(12)	22.8(4)	1.9
O7	7467.0(17)	8639.3(18)	1837.5(13)	26.9(4)	2.1
O8	8803.9(16)	10078.1(18)	1192.3(13)	23.2(4)	2.1
O9	6848.2(17)	9986(2)	734.7(14)	30.9(5)	1.9
F1	6279.8(18)	2880.8(18)	5579.8(14)	46.1(5)	0.8
F2	5910.7(14)	4290.9(18)	4513.6(11)	33.5(4)	1.1

[a]U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

[b]Bond valence sums are calculated by using bond valence theory (Si = $\exp[(R_o-R_i)/B]$, where R_o is an empirical constant, R_i is the length of bond I (in angstroms), and B = 0.37).[10-11]

Table 3 Selected bond lengths [Å] and angles [°] for $(NH_4)_2B_6O_9F_2$ and $K_2B_6O_9F_2$.

$(NH_4)_2B_6O_9F_2$			
B1-O1	1.364(3)	O2-B1-O1	122.62(19)
B1-O2	1.346(3)	O2-B1-O3	121.17(18)
B1-O3	1.393(3)	F1-B2-O2	108.43(16)
B2-O2	1.451(3)	F1-B2-O4	107.51(17)
B2-O4	1.475(3)	F1-B2-O9	106.67(16)
B2-O9	1.468(3)	O2-B2-O4	112.21(17)
B2-F1	1.429(3)	O2-B2-O9	112.46(18)
B3-O3	1.385(3)	O9-B2-O4	109.29(16)
B3-O4	1.349(3)	O4-B3-O3	121.65(18)
B3-O5	1.372(3)	O4-B3-O5	122.92(18)
B4-O5	1.382(3)	O5-B3-O3	115.39(18)
B4-O7	1.380(3)	O6-B4 -O5	122.29(19)
B5-O1	1.464(3)	O6-B4 -O7	121.93(19)
B5-O8	1.452(3)	O7-B4-O5	115.75(19)
B5#1-O6	1.464(3)	F2-B5-O1	105.29(16)
B5-O6#4	1.464(3)	F2-B5-O6#4	107.54(17)
B5-F2	1.425(3)	F2-B5-O8	108.16(16)
B6#2-O7	1.393(3)	O1-B5-O6#4	110.27(16)
B6-O7#5	1.393(3)	O8-B5-O1	112.64(18)
B6#3-O8	1.351(3)	O8-B5-O6#4	112.52(17)
B6-O8#6	1.351(3)	O8#6-B6-O7#5	120.82(19)
B6-O9	1.362(3)	O8#6-B6-O9	123.53(19)
O1-B1-O3	116.21(18)	O9-B6-O7#5	115.65(18)
$K_2B_6O_9F_2$			
K1#8-O1	2.8087(19)	K2-O6#3	3.066(2)
K1-O1#5	2.8087(19)	K2#4-F1	2.834(2)
K1-O2#5	3.369(2)	K2-F1#4	2.834(2)
K1#8-O2	3.369(2)	K2-F2	2.5928(19)
K1-O4#2	3.004(2)	B1-O1	1.434(3)
K1#1-O4	3.004(2)	B1-O8#14	1.438(3)
K1-O6#2	3.280(2)	B1#13-O8	1.438(3)
K1#1-O6	3.280(2)	B1-F1	1.395(3)
K1-O7#7	2.752(2)	B1-F2	1.426(3)
K1#12-O7	2.752(2)	B2-O1	1.344(3)
K1-O8#7	2.816(2)	B2-O2	1.347(3)
K1#12-O8	2.816(2)	B2-O3	1.396(3)
K1#9-O9	2.7137(19)	B3-O2	1.450(4)
K1-O9#6	2.7138(19)	B3-O6#15	1.483(3)
K1-F1	3.253(2)	B3#10-O9	1.461(4)
K1-F2	2.6249(19)	B3-O9#15	1.461(4)
K2-O1#1	3.4234(19)	B3#10-O6	1.483(3)
K2#2-O1	3.4235(19)	B4-O4	1.343(4)

K2-O2#1	2.6957(19)	B4-O3	1.371(3)
K2#2-O2	2.6958(19)	B4-O5	1.371(3)
K2-O3	2.806(2)	B5-O5	1.377(3)
K2-O4#3	2.686(2)	B5-O6	1.349(4)
K2#11-O4	2.686(2	B5-O7	1.368(4)
K2-O5	2.998(2)	B6-O7	1.402(3)
K2#1-O6	3.410(2)	B6-O8	1.347(4)
K2#11-O6	3.066(2)	B6-O9	1.346(4)
K2-O6#2	3.410(2)		
O9#6-K1-O1#5	63.67(6)	O4#2-K2-O6#2	66.88(5)
O9#6-K1-O2#5	74.18(5)	O4#2-K2-O3	116.77(6)
O9#6-K1-O6#3	104.60(6)	O4#2-K2-F1#4	94.89(6)
O9#6-K1-O4#3	48.49(5)	O4#2-K2-O5	99.94(6)
O9#6-K1-O7#7	96.65(6)	O3-K2-O1#1	72.70(5)
O9#6-K1-F1	110.79(6)	O3-K2-O6#3	78.85(5)
O9#6-K1-O8#7	137.97(6)	O3-K2-O6#2	142.18(6)
O6#3-K1-O2#5	149.27(5)	O3-K2-F1#4	143.83(7)
O4#3-K1-O2#5	102.20(5)	O3-K2-O5	46.52(5)
O4#3-K1-O6#3	60.74(5)	F1#4-K2-O1#1	88.11(6)
O4#3-K1-F1	100.92(5)	F1#4-K2-O6#2	64.68(5)
O7#7-K1-O1#5	90.84(6)	F2#4-K2-O1#1	100.40(5)
O7#7-K1-O2#5	132.66(6)	F2-K2-O2#1	130.39(6)
O7#7-K1-O6#3	78.03(6)	F2-K2-O6#2	154.10(6)
O7#7-K1-O4#3	105.25(6)	F2-K2-O6#3	69.64(5)
O7#7-K1-F1	150.60(6)	F2-K2-O4#2	108.12(6)
O7#7-K1-O8#7	49.02(6)	F2-K2-O3	63.54(5)
O8#7-K1-O2#5	109.33(6)	F2-K2-F1#4	91.34(6)
O8#7-K1-O6#3	92.17(6)	F2-K2-O5	109.94(6)
O8#7-K1-O4#3	148.22(6)	F1#4-K2-O6#3	118.20(6)
O8#7-K1-F1	101.72(6)	F1#4-K2-O5	148.45(6)
O1#5-K1-O2#5	42.97(5)	O1-B2-O2	119.3(2)
O1#5-K1-O6#3	163.08(6)	O1-B2-O3	120.8(2)
O1#5-K1-O4#3	111.24(5)	O2-B2-O3	119.9(2)
O1#5-K1-F1	92.01(5)	F2-B1-O1	110.8(2)
O1#5-K1-O8#7	89.96(6)	F2-B1-O8#14	107.1(2)
F1-K1-O2#5	51.36(4)	O1-B1-O8#14	115.4(2)
F1-K1-O6#3	103.96(5)	F1-B1-F2	104.9(2)
F2-K1-O1#5	125.13(6)	F1-B1-O1	108.9(2)
F2-K1-O2#5	92.37(5)	F1-B1-O8#14	109.2(2)
F2-K1-O9#6	146.34(6)	O4-B4-O3	122.4(2)
F2-K1-O6#3	71.54(5)	O4-B4-O5	123.7(2)
F2-K1-O4#3	107.68(6)	O3-B4-O5	113.9(2)
F2-K1-O7#7	114.43(6)	O6-B5-O7	122.8(2)
F2-K1-F1	43.08(5)	O6-B5-O5	123.2(3)

F2-K1-O8#7	75.43(6)	O7-B5-O5	114.0(2)
O2#1-K2-O1#1	42.56(5)	O2-B3-O9#15	111.0(2)
O2#1-K2-O6#3	159.29(6)	O2-B3-O6#15	108.3(2)
O2#1-K2-O6#2	48.22(5)	O2-B3-O4	110.4(2)
O2#1-K2-O3	113.14(6)	O9#15-B3-O6#15	111.4(2)
O2#1-K2-F1#4	62.52(6)	O9#15-B3-O4	106.1(2)
O2#1-K2-O5	85.95(6)	O6#15-B3-O4	109.6(2)
O6#3-K2-O1#1	151.26(5)	O9-B6-O7	119.6(3)
O62-K2-O1#1	88.99(5)	O9-B6-O8	126.0(3)
O4#2-K2-O2#1	115.06(6)	O8-B6-O7	114.4(3)
O4#2-K2-O6#3	45.17(5)		

Symmetry transformations used to generate equivalent atoms:

$(NH_4)_2B_6O_9F_2$		$K_2B_6O_9F_2$	
#1 − x, − 1/2 + y, − 1/2 − z	#1 3/2 − x, 1/2 + Y, + z	#7 1 − x, − 1/2 + y,1/2 − z	#13 x, 3/2 − y, −1/2 + z
#2 1 − x, − 1/2 + y, − 1/2 − z	#2 − 1/2 + x, + y, 1/2 − z	#8 1/2 + x, 1/2 − y, 1 − z	#14 x, 3/2 − y, 1/2 + z
#3 − 1 + x, y, z	#3 3/2 − x, − 1/2 + y, z	#9 2 − x, 1/2 + y, 1/2 − Z	#15 2 − x, − 1/2 + y, 1/2 − z
#4 − x, 1/2 + y, −1/2 − z	#4 1 − x, 1 − y, 1 − z	#10 1/2 + x, 1 + y, 1/2 − z	
#5 1 − x, 1/2 + y, −1/2 − z	#5 1/2 + x, 1/2 − y, 1 − z	#11 1/2 + x, + y, 1/2 − z	
#6 1 + x, y, z	#6 − 1/2 + x, −1 + y, 1/2 − z	#12 1 − x, 1/2 + y, 1/2 − z	

Table S4 Hydrogen bonds for $(NH_4)_2B_6O_9F_2$. D, hydrogen bond donor; A, hydrogen bond acceptor.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1A...O1	0.98(3)	1.78(3)	2.754(2)	171.6(3)
N1-H1A...F2#1	0.98(4)	2.59(4)	3.164(2)	117.2(3)
N1-H1B...F2#2	0.91(4)	1.95(4)	2.812(2)	156.6(3)
N1-H1C...O1#3	0.88(3)	2.83(3)	3.346(2)	118.7(3)
N1-H1C...O6	0.88(3)	2.13(4)	3.000(2)	167.5(3)
N1-H1D...F1	0.94(5)	2.11(5)	2.983(3)	154.0(3)
N1-H1D...O5#4	0.94(2)	2.87(2)	3.377(3)	115.4(3)
N2-H2A...O9#5	0.96(3)	1.88(3)	2.821(3)	166.3(3)
N2-H2B...F1#6	0.93(4)	1.89(4)	2.792(2)	161.2(3)
N2-H2C...O4	0.87(4)	2.24(4)	3.079(2)	162.8(3)
N2-H2C...O6	0.87(4)	2.61(4)	3.175(2)	124.1(3)
N2-H2D...F2#3	1.02(4)	2.38(4)	3.084(2)	125.3(3)
N2-H2D...O3#3	1.02(4)	2.23(4)	3.163(2)	152.6(3)

Symmetry transformations used to generate equivalent atoms:

#1 $1 + x, -1/2 - y, 1/2 + z$;   #2 $-1 - X, -1/2 + y, -1/2 - z$;   #3 $-x, -1/2 + y, -1/2 - z$;

#4 $x, -1/2 - y, 1/2 + z$;   #5 $1 - x, -y, -z$;   #6 $1 + x, y, z$

Table S5 Assignment of infrared absorption peaks of $(NH_4)_2B_6O_9F_2$.[12-14]

Vibration mode description of characteristic absorption peak	Wavenumber (cm^{-1})
N-H stretching vibration	3282, 3216
B_3-O asymmetric stretching vibrations	1525, 1422, 1336
B-F asymmetric stretching vibrations	1232, 1225, 1110
B_3-O symmetric stretching vibrations	974, 902, 867
B-F symmetric stretching vibrations	767, 707
B_3-O out-of-plane bending vibrations	814, 758, 692
B_3-O bending vibrations	578, 539, 492, 435

Table S6 Comparison of the maternal compound LiB_3O_5 and the $A_2B_6O_9F_2$ family in terms of the constituent anionic groups, dimension and birefringence.

Compounds		Anionic groups	Dimension	Birefringence (Δn_{cal} at 1064 nm)	Ref.
The maternal compound	LiB_3O_5	$[BO_3]$, $[BO_4]$	3D	0.040	[15]
The $A_2B_6O_9F_2$ family	$Na_2B_6O_9F_2$	$[BO_3]$, $[BO_3F]$	2D	0.064	[16]
	$NaKB_6O_9F_2$	$[BO_3]$, $[BO_4]$, $[BO_2F_2]$		0.053	[17]
	$NaRbB_6O_9F_2$	$[BO_3]$, $[BO_4]$, $[BO_2F_2]$		0.053	[18]
	$(NH_4)_2B_6O_9F_2$	$[BO_3]$, $[BO_3F]$		0.050	This work
	$K_2B_6O_9F_2$	$[BO_3]$, $[BO_4]$, $[BO_2F_2]$		0.053	
	$Li_2B_6O_9F_2$	$[BO_3]$, $[BO_4]$, $[BO_2F_2]$	3D	0.070	[19,20]
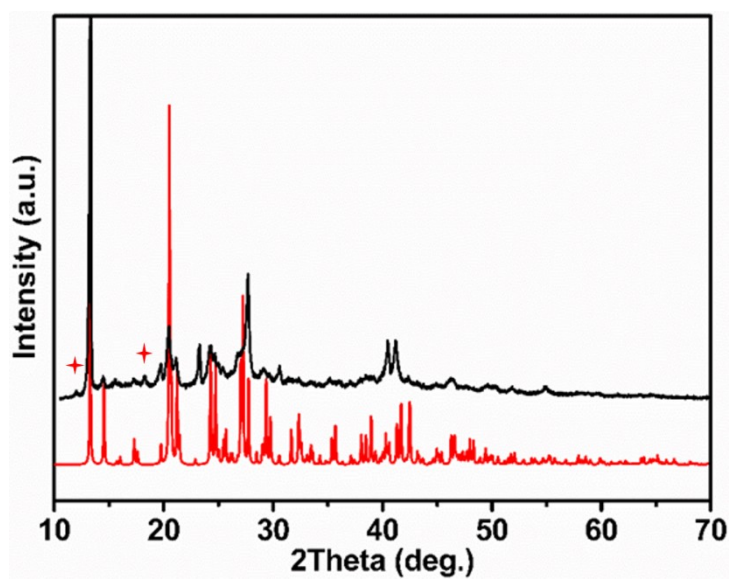
Figure S1 Calculated and experimental powder X-ray diffraction patterns of $(NH_4)_2B_6O_9F_2$. A bit of impurity has been marked, which cannot be removed via washing the crystals with anhydrous ethanol or acetone.
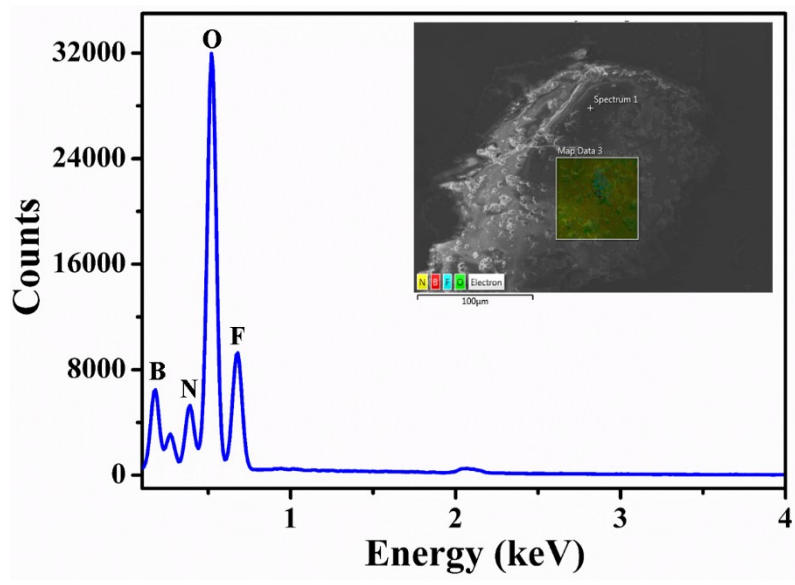
Figure S2 EDS analysis of $(NH_4)_2B_6O_9F_2$.

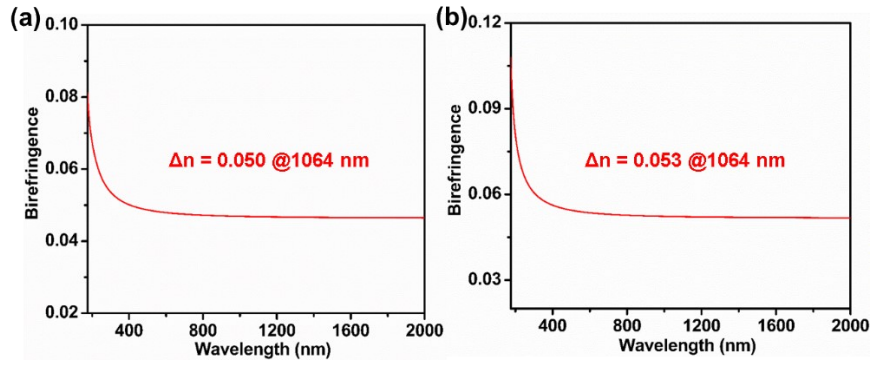Figure S3 The calculated birefringence of $(NH_4)_2B_6O_9F_2$ (a) and $K_2B_6O_9F_2$ (b).

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