Supplementary Information

Deep ultraviolet transparent borophosphates $LiAB_2P_2O_9$ (A = NH_4, K) and $LiNaB_2P_2O_8(OH)_2 \cdot H_2O$ exhibiting a moderate second-harmonic generation response

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Experimental section

Crystal growth and solid states synthesis

Single crystals of $LiAB_2P_2O_9$ (A = NH_4, K) and $LiNaB_2P_2O_8(OH)_2 \cdot H_2O$ were grown by the solid-state reaction in a closed system. The initial reagents of LiCl, H_3BO_3, $NH_4H_2PO_4/KH_2PO_4$ (KDP)/NaH_2PO_4 were blended thoroughly in an agate mortar with a molar ratio of 14: 3: 8, 1: 2: 2, 1: 2: 2, respectively. The above raw materials were respectively encapsulated in a 23 mL hydrothermal kettle with polytetrafluoroethylene lining and put into a drying oven with programmed temperature control. The temperature was brought up to 220 ℃ in 120 min and maintained for 72 h, cooling to 190 ℃ in 1800 min, 150 ℃ in 1600 min, 120 ℃ in 700 min, and 90 ℃ in 510 min, and it was cooled to room temperature after 480 min.

The $LiAB_2P_2O_9$ (A = NH_4, K) polycrystalline powders were synthesized by solid-state reaction technique in a closed system. By the temperature of the crystal growth, LiCl, H_3BO_3, and $NH_4H_2PO_4/KH_2PO_4$ are thoroughly ground and mixed in stoichiometric ratios. However, we made multiple attempts, but were only able to obtain the crystal for the structure of $LiNaB_2P_2O_8(OH)_2 \cdot H_2O$ rather than the pure polycrystalline powder sample.

Structure determination

Single-crystal XRD data of the title compounds were collected on a Bruker D8 Venture diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 293.15 K. Data absorption correction of the data was completed by SAINT-Plus software.[1] The structure of the title crystal was solved with programs from the SHELXTL crystallographic software package with the Olex2 software.[2] The symmetry of the structures was checked by the PLATON program, and no higher symmetry was found.[3] The crystal data and structure refinement information for $LiAB_2P_2O_9$ (A = NH_4, K) and $LiNaB_2P_2O_8(OH)_2 \cdot H_2O$ are listed in Table S1. The equivalent isotropic displacement parameters and atomic coordinates of the three compounds are summarized in Table S2, and Table S3 contains a list of the selected bond lengths and angles.

Powder X-ray diffraction.

The powder X-ray diffraction (XRD) patterns of $LiAB_2P_2O_9$ (A = NH_4, K) were measured using a Bruker D2 PHASER X-ray diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å). The scanning range of 2θ was set from 5 to 70° with a fixed counting time of 1 s/step and a scan step width of 0.02°, respectively.

Infrared and UV–Vis–NIR diffuse reflectance spectra

The Shimadzu IR Affinity-1 Fourier transform infrared spectrometer was utilized to measure the infrared spectra within the 4000-400 cm^{-1} range. The samples and dried KBr were thoroughly mixed. At room temperature, the Shimadzu SolidSpec-3700DUV spectrophotometer was used to measure the diffuse reflectance spectra, and the data were recorded in the wavelength range of 200-2600 nm.

Thermal analysis

Thermogravimetric-differential scanning calorimetry (TG-DSC) analysis was employed to measure the thermodynamic properties of $LiAB_2P_2O_9$ (A = NH_4, K) by a simultaneous thermal analyzer (NETZSCH STA 449 F3) under a flowing N_2 atmosphere. The samples ($LiNH_4B_2P_2O_9$: 4.03 mg, $LiKB_2P_2O_9$: 6.49 mg) were placed in the Pt crucibles from 40-800 °C, and the heating and cooling rates were 5 °C/min.

Powder second harmonic generation (SHG) measurements

Powder SHG tests were measured by a modified Kurtz–Perry method using a Q-switched Nd: YVO_4 solid-state laser at 1064 nm and 532 nm for visible and ultraviolet SHG, respectively. Polycrystalline $LiAB_2P_2O_9$ (A = NH_4, K) samples were ground and sieved into the following particle size ranges: 20-38, 38-55, 55-88, 88-105, 105-150 and 150-200 μm. 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. Then the samples were irradiated with a pulsed laser, and the second harmonic output was separated by a narrowband pass filter (530 ± 10 nm) and detected by a photomultiplier tube attached to an oscilloscope. No index-matching fluid was used in any of the experiments.

Birefringence measurements

A block single crystal with a thickness determined on a single-crystal XRD diffractometer was chosen to test birefringence with a cross-polarizing microscope (NIKON Eclipse Ci-POL) equipped with a quartz wedge compensator under a 546 nm light source. The birefringence was determined using the formula R (retardation) = $|N_g - N_p| \times d = \Delta n \times d$, where N_g, N_p, and Δn denote the refractive indices of fast light, slow light, and the birefringence, respectively. R represents the optical path difference, while d signifies the thickness of the crystal.

Theoretical calculations

The electronic structures as well as linear optical property calculations were performed by employing CASTEP, a plane-wave pseudopotential density functional theory (DFT) package, with the norm-conserving pseudopotentials (NCPs).[4, 5] The

related calculations are performed by Perdew−Burke−Ernzerhof (PBE) functional under the generalized gradient approximation (GGA).[6] The plane-wave energy cutoff was set at 750 eV. Self-consistent field (SCF) calculations were performed with a convergence criterion of 5×10^{-7} eV/atom on the total energy. Using the Monkhorst-Pack method, the *k* point sampling was finally set as 4 × 3 × 2. The nonlocal exchange functional Heyd-Scuseria-Ernzerhof (HSE06) was adopted to calculate bandgaps. The band gap differences between the GGA-PBE and HSE06 methods were utilized as scissor operators to enhance the accuracy of calculations for birefringence and SHG coefficients.[7]

$$E_{xc}^{HSE} = aE_{x}^{HF,SR}(w) + (1 - a)E_{x}^{PBE,SR}(w) + E_{x}^{PBE,LR}(w) + E_{c}^{PBE}(w)$$

The valence electrons of the elements in title compounds were calculated as follows: Li ($2s^1$), N ($2s^22p^3$), K ($3s^23p^64s^1$), Na ($2s^22p^63s^1$), B ($2s^22p^1$), P ($3s^23p^3$), O ($2s^22p^4$), respectively.

Table S1. Crystal data and structure refinement for $LiNH_4B_2P_2O_9$, $LiKB_2P_2O_9$ and $LiNaB_2P_2O_8(OH)_2 \cdot H_2O$.

Empirical formula	$LiNH_4B_2P_2O_9$	$LiKB_2P_2O_9$	$LiNaB_2P_2O_8(OH)_2 \cdot H_2O$
Formula weight	252.54	273.6	293.52
Temperature (K)	293	293	293
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$C2$
a (Å)	7.1922(5)	7.1528(5)	12.5422(12)
b (Å)	7.3988(5)	7.3764(7)	7.9359(8)
c (Å)	12.7559(9)	12.6353(13)	4.2826(4)
β (°)	90	90	107.839(4)
Volume (Å^3)	678.79(8)	666.66(10)	405.77(7)
Z	4	4	2
ρ_{calc} (g/cm^3)	2.471	2.726	2.402
μ (mm^{-1})	0.678	1.307	0.646
F(000)	504	536	292
2θ range for data collection (°)	6.366 to 54.964	6.396 to 55.022	6.164 to 54.928
Index ranges	$-9 \le h \le 9$, $-9 \le k \le 9$, $-15 \le l \le 16$	$-9 \le h \le 8$, $-9 \le k \le 9$, $-16 \le l \le 16$	$-16 \le h \le 16$, $-10 \le k \le 9$, $-5 \le l \le 5$
Reflections collected	5431	5434	3000
Independent reflections	1554 [$R_{int} = 0.0596$]	1531 [$R_{int} = 0.0747$]	874 [$R_{int} = 0.0655$]
Completeness (%)	99.60	99.70	97.70
Data/restraints/parameters	1554/3/153	1531/0/136	874/3/88
Goodness-of-fit on F^2	1.11	1.061	1.101
Final R indexes [$I \ge 2\sigma(I)$]	$R_1 = 0.0363$, $wR_2 = 0.0806$	$R_1 = 0.0414$, $wR_2 = 0.0952$	$R_1 = 0.0336$, $wR_2 = 0.0669$
Final R indexes [all data]	$R_1 = 0.0406$, $wR_2 = 0.0829$	$R_1 = 0.0445$, $wR_2 = 0.0993$	$R_1 = 0.0364$, $wR_2 = 0.0701$
Largest diff. peak (hole·e Å^{-3})	0.49/-0.51	0.49/-0.65	0.30/-0.37
Flack parameter	-0.09(10)	-0.01(6)	-0.06(12)

Table S2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $LiNH_4B_2P_2O_9$, $LiKB_2P_2O_9$ and $LiNaB_2P_2O_8(OH)_2 \cdot H_2O$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	Wyck.	*x*	*y*	*z*	*U*(eq)	BVS
			$LiNH_4B_2P_2O_9$			
Li1	4a	8917(13)	3949(11)	2606(7)	22.0(18)	0.98
B1	4a	2636(7)	5444(7)	2479(4)	9.8(10)	3.05
B2	4a	2345(7)	3469(7)	4028(4)	8.7(10)	3.05
P1	4a	6011.2(17)	7114.8(17)	2664.2(9)	12.0(3)	5.25
P2	4a	4629.8(16)	4173.0(16)	5772.6(9)	9.5(3)	5.18
O1	4a	3954(4)	6768(4)	2921(2)	11.7(7)	2.04
O2	4a	1483(4)	6552(4)	1739(2)	11.4(7)	2.15
O3	4a	3641(4)	4029(4)	1873(2)	12.0(7)	1.95
O4	4a	1499(4)	4649(4)	3272(2)	9.5(7)	1.89
O5	4a	906(5)	2394(4)	4570(2)	12.0(7)	2.02
O6	4a	3742(4)	2265(5)	3536(2)	12.1(7)	2.00
O7	4a	3286(4)	4555(4)	4860(2)	10.5(7)	2.00
O8	4a	5635(4)	5860(5)	6082(3)	14.2(7)	2.00
O9	4a	7237(5)	5720(5)	3135(3)	19.7(8)	2.01
			$LiKB_2P_2O_9$			
Li1	4a	8862(13)	3933(14)	2581(8)	19(2)	0.97
K1	4a	9171.3(16)	6073.3(18)	5030.3(11)	21.4(3)	1.16
B1	4a	2612(7)	5417(7)	2462(5)	8.7(12)	3.03
B2	4a	2340(7)	3447(7)	4027(5)	8.1(11)	3.05
P1	4a	6018.5(18)	7069.3(19)	2682.0(12)	11.0(3)	5.24
P2	4a	-339.1(16)	792.4(18)	4254.8(11)	8.6(3)	5.20
O1	4a	7242(5)	5693(6)	3185(3)	18.7(9)	2.00
O2	4a	3948(5)	6748(5)	2919(3)	10.6(8)	2.16
O3	4a	3650(5)	4008(5)	1853(3)	13.2(8)	2.10
O4	4a	1454(5)	6515(5)	1722(3)	10.5(8)	2.16
O5	4a	1462(4)	4604(5)	3260(3)	8.9(7)	1.96
O6	4a	3293(4)	4589(4)	4833(3)	9.5(7)	2.12
O7	4a	3714(5)	2209(5)	3532(3)	11.5(8)	2.07
O8	4a	897(5)	2393(5)	4601(3)	10.5(8)	2.11

O9	4a	704(5)	-892(5)	3968(3)	13.2(8)	2.01
$LiNaB_2P_2O_8(OH)_2 \cdot H_2O$						
Li1	2b	5000	7568(14)	5000	16(2)	1.12
Na1	2a	5000	3974(4)	10000	39.0(9)	0.88
B1	4c	2157(4)	4021(6)	-1505(11)	11.2(9)	3.05
P1	4c	2816.8(8)	5937.4(13)	4112(2)	9.1(3)	5.21
O1	4c	1066(3)	3647(4)	-1310(8)	13.7(7)	1.98
O2	4c	1965(2)	5271(4)	-4229(7)	12.0(6)	1.97
O3	4c	2763(2)	2538(4)	-2324(7)	12.0(6)	2.01
O4	4c	2950(2)	4658(4)	1543(6)	12.1(7)	2.09
O5	4c	3946(2)	6261(4)	6522(7)	13.8(7)	1.88
O6	2b	5000	2437(7)	5000	31.2(12)	1.86

Table S3. Bond lengths and angles for $LiNH_4B_2P_2O_9$, $LiKB_2P_2O_9$ and $LiNaB_2P_2O_8(OH)_2 \cdot H_2O$.

$LiNH_4B_2P_2O_9$			
Li(1)-O(2)$^{\#1}$	1.982(9)	B(2)-O(6)	1.482(6)
Li(1)-O(4)$^{\#3}$	2.107(10)	B(2)-O(7)	1.494(6)
Li(1)-O(8)$^{\#2}$	1.975(9)	P(1)-O(1)	1.537(3)
Li(1)-O(9)	1.906(9)	P(1)-O(3)$^{\#4}$	1.555(3)
B(1)-O(1)	1.475(6)	P(1)-O(6)$^{\#4}$	1.546(3)
B(1)-O(2)	1.500(6)	P(1)-O(9)	1.484(4)
B(1)-O(3)	1.488(6)	P(2)-O(2)$^{\#6}$	1.565(3)
B(1)-O(4)	1.427(6)	P(2)-O(5)$^{\#7}$	1.542(3)
B(2)-O(4)	1.436(6)	P(2)-O(7)	1.539(3)
B(2)-O(5)	1.477(6)	P(2)-O(8)	1.495(3)
O(2)$^{\#1}$-Li(1)-O(4)$^{\#3}$	100.2(4)	O(5)-B(2)-O(6)	110.5(4)
O(8)$^{\#2}$-Li(1)-O(2)$^{\#1}$	120.2(5)	O(5)-B(2)-O(7)	105.9(4)
O(8)$^{\#2}$-Li(1)-O(4)$^{\#3}$	103.6(4)	O(6)-B(2)-O(7)	108.5(4)
O(9)-Li(1)-O(2)$^{\#1}$	111.9(4)	O(1)-P(1)-O(3)$^{\#4}$	103.09(18)
O(9)-Li(1)-O(4)$^{\#3}$	104.3(4)	O(1)-P(1)-O(6)$^{\#4}$	109.49(18)
O(9)-Li(1)-O(8)$^{\#2}$	113.7(5)	O(6)$^{\#4}$-P(1)-O(3)$^{\#4}$	106.97(19)
O(1)-B(1)-O(2)	103.4(4)	O(9)-P(1)-O(1)	111.7(2)
O(1)-B(1)-O(3)	110.7(4)	O(9)-P(1)-O(3)$^{\#4}$	112.6(2)
O(3)-B(1)-O(2)	109.0(4)	O(9)-P(1)-O(6)$^{\#4}$	112.5(2)
O(4)-B(1)-O(1)	111.8(4)	O(5)$^{\#7}$-P(2)-O(2)$^{\#6}$	105.68(18)
O(4)-B(1)-O(2)	110.8(4)	O(7)-P(2)-O(2)$^{\#6}$	109.71(18)
O(4)-B(1)-O(3)	110.9(4)	O(7)-P(2)-O(5)$^{\#7}$	107.30(18)
O(4)-B(2)-O(5)	110.2(4)	O(8)-P(2)-O(2)$^{\#6}$	109.02(18)
O(4)-B(2)-O(6)	111.6(4)	O(8)-P(2)-O(5)$^{\#7}$	114.50(19)
O(4)-B(2)-O(7)	110.0(4)	O(8)-P(2)-O(7)	110.48(19)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, y-1/2, -z+1/2 #2 -x+3/2, -y+1, z-1/2 #3 x+1, y, z

#4 -x+1, y+1/2, -z+1/2 #5 -x+3/2, -y+1, z+1/2 #6 -x+1/2, -y+1, z+1/2

#7 x+1/2, -y+1/2, -z+1 #8 -x+1/2, -y+1, z-1/2 #9 x-1, y, z

#10 x-1/2, -y+1/2, -z+1

$LiKB_2P_2O_9$			
Li(1)-O(1)	1.900(11)	B(1)-O(4)	1.489(6)

Li(1)-O(4)$^{\#3}$	2.002(11)	B(1)-O(5)	1.433(6)
Li(1)-O(5)$^{\#5}$	2.107(11)	B(2)-O(5)	1.436(7)
Li(1)-O(9)$^{\#4}$	1.986(11)	B(2)-O(6)	1.487(6)
K(1)-O(1)	2.724(4)	B(2)-O(7)	1.480(6)
K(1)-O(2)$^{\#6}$	3.053(4)	B(2)-O(8)	1.483(6)
K(1)-O(3)$^{\#7}$	2.781(4)	P(1)-O(1)	1.483(4)
K(1)-O(5)$^{\#5}$	2.977(4)	P(1)-O(2)	1.530(4)
K(1)-O(6)$^{\#6}$	3.266(4)	P(1)-O(3)$^{\#4}$	1.564(4)
K(1)-O(6)$^{\#5}$	3.155(3)	P(1)-O(7)$^{\#4}$	1.549(4)
K(1)-O(7)$^{\#8}$	3.044(4)	P(2)-O(4)$^{\#14}$	1.563(4)
K(1)-O(8)$^{\#5}$	3.031(4)	P(2)-O(6)$^{\#13}$	1.538(4)
K(1)-O(9)$^{\#8}$	2.788(4)	P(2)-O(8)	1.538(4)
K(1)-O(9)$^{\#9}$	2.831(4)	P(2)-O(9)	1.494(4)
B(1)-O(2)	1.487(6)	O(8)$^{\#5}$-K(1)-O(6)$^{\#5}$	45.12(9)
O(1)-Li(1)-O(2)$^{\#3}$	92.8(4)	O(8)$^{\#5}$-K(1)-O(6)$^{\#6}$	164.89(10)
O(1)-Li(1)-O(4)$^{\#3}$	111.3(5)	O(8)$^{\#5}$-K(1)-O(7)$^{\#8}$	55.82(10)
O(1)-Li(1)-O(5)$^{\#5}$	102.4(5)	O(9)$^{\#8}$-K(1)-O(2)$^{\#6}$	66.01(10)
O(1)-Li(1)-O(9)$^{\#4}$	116.6(5)	O(9)$^{\#9}$-K(1)-O(2)$^{\#6}$	90.36(11)
O(4)$^{\#3}$-Li(1)-O(2)$^{\#3}$	58.5(3)	O(9)$^{\#8}$-K(1)-O(5)$^{\#5}$	144.42(11)
O(4)$^{\#3}$-Li(1)-O(5)$^{\#5}$	97.4(4)	O(9)$^{\#9}$-K(1)-O(5)$^{\#5}$	73.66(11)
O(5)$^{\#5}$-Li(1)-O(2)$^{\#3}$	155.3(5)	O(9)$^{\#9}$-K(1)-O(6)$^{\#5}$	82.83(10)
O(9)$^{\#4}$-Li(1)-O(2)$^{\#3}$	85.6(4)	O(9)$^{\#8}$-K(1)-O(6)$^{\#6}$	81.48(10)
O(9)$^{\#4}$-Li(1)-O(4)$^{\#3}$	120.6(6)	O(9)$^{\#8}$-K(1)-O(6)$^{\#5}$	148.28(11)
O(9)$^{\#4}$-Li(1)-O(5)$^{\#5}$	104.4(5)	O(9)$^{\#9}$-K(1)-O(6)$^{\#6}$	47.52(10)
O(1)-K(1)-O(2)$^{\#6}$	138.95(12)	O(9)$^{\#8}$-K(1)-O(7)$^{\#8}$	66.13(10)
O(1)-K(1)-O(3)$^{\#7}$	172.07(13)	O(9)$^{\#9}$-K(1)-O(7)$^{\#8}$	162.43(11)
O(1)-K(1)-O(5)$^{\#5}$	66.30(10)	O(9)$^{\#9}$-K(1)-O(8)#5	117.76(11)
O(1)-K(1)-O(6)$^{\#6}$	92.78(11)	O(9)$^{\#8}$-K(1)-O(8)$^{\#5}$	113.62(11)
O(1)-K(1)-O(6)$^{\#5}$	111.72(12)	O(9)$^{\#8}$-K(1)-O(9)$^{\#9}$	126.70(9)
O(1)-K(1)-O(7)$^{\#8}$	111.99(12)	O(2)-B(1)-O(3)	109.9(4)
O(1)-K(1)-O(8)$^{\#5}$	87.77(12)	O(2)-B(1)-O(4)	104.0(4)
O(1)-K(1)-O(9)$^{\#8}$	86.16(12)	O(4)-B(1)-O(3)	109.4(4)
O(1)-K(1)-O(9)$^{\#9}$	82.63(12)	O(5)-B(1)-O(2)	111.8(4)
O(2)$^{\#6}$-K(1)-O(6)$^{\#5}$	107.37(10)	O(5)-B(1)-O(3)	110.9(4)

O(2)$^{\#6}$-K(1)-O(6)$^{\#6}$	55.20(10)	O(5)-B(1)-O(4)	110.5(4)
O(3)$^{\#7}$-K(1)-O(2)$^{\#6}$	48.54(10)	O(5)-B(2)-O(6)	109.1(4)
O(3)$^{\#7}$-K(1)-O(5)$^{\#5}$	107.82(11)	O(5)-B(2)-O(7)	111.8(5)
O(3)$^{\#7}$-K(1)-O(6)$^{\#6}$	94.88(11)	O(5)-B(2)-O(8)	109.7(4)
O(3)$^{\#7}$-K(1)-O(6)$^{\#5}$	62.25(11)	O(7)-B(2)-O(6)	109.6(4)
O(3)$^{\#7}$-K(1)-O(7)$^{\#8}$	63.20(11)	O(7)-B(2)-O(8)	110.2(4)
O(3)$^{\#7}$-K(1)-O(8)$^{\#5}$	84.30(11)	O(8)-B(2)-O(6)	106.3(4)
O(3)$^{\#7}$-K(1)-O(9)$^{\#8}$	96.98(11)	O(1)-P(1)-O(2)	112.4(2)
O(3)$^{\#7}$-K(1)-O(9)$^{\#9}$	101.10(11)	O(1)-P(1)-O(3)$^{\#4}$	112.0(2)
O(5)$^{\#5}$-K(1)-O(2)$^{\#6}$	149.10(10)	O(1)-P(1)-O(7)$^{\#4}$	113.4(2)
O(5)$^{\#5}$-K(1)-O(6)$^{\#5}$	45.58(10)	O(2)-P(1)-O(3)$^{\#4}$	102.4(2)
O(5)$^{\#5}$-K(1)-O(6)$^{\#6}$	120.15(10)	O(2)-P(1)-O(7)$^{\#4}$	108.9(2)
O(5)$^{\#5}$-K(1)-O(7)$^{\#8}$	102.59(11)	O(7)$^{\#4}$-P(1)-O(3)$^{\#4}$	107.0(2)
O(5)$^{\#5}$-K(1)-O(8)$^{\#5}$	46.80(10)	O(6)$^{\#13}$-P(2)-O(4)$^{\#14}$	109.22(19)
O(6)$^{\#5}$-K(1)-O(6)$^{\#6}$	121.61(10)	O(6)$^{\#13}$-P(2)-O(8)	107.0(2)
O(7)$^{\#8}$-K(1)-O(2)$^{\#6}$	84.64(11)	O(8)-P(2)-O(4)$^{\#14}$	104.8(2)
O(7)$^{\#8}$-K(1)-O(6)$^{\#6}$	136.64(11)	O(9)-P(2)-O(4)$^{\#14}$	110.3(2)
O(7)$^{\#8}$-K(1)-O(6)$^{\#5}$	82.62(10)	O(9)-P(2)-O(6)$^{\#13}$	110.3(2)
O(8)$^{\#5}$-K(1)-O(2)$^{\#6}$	130.13(11)	O(9)-P(2)-O(8)	114.8(2)
B(1)-O(3)	1.491(7)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2, y-1/2, -z+1/2 #2 -x+3/2, -y+1, z-1/2 #3 -x+1, y-1/2, -z+1/2

#4 -x+1, y+1/2, -z+1/2 #5 x+1, y, z #6 x+1/2, -y+3/2, -z+1

#7 -x+3/2, -y+1, z+1/2 #8 x+1/2, -y+1/2, -z+1 #9 x+1, y+1, z

#10 x-1, y, z #11 x-1/2, -y+3/2, -z+1 #12 x-1, y-1, z

#13 x-1/2, -y+1/2, -z+1 #14 -x, y-1/2, -z+1/2 #15 -x, y+1/2, -z+1/2

$LiNaB_2P_2O_8(OH)_2 \cdot H_2O$

Li(1)-O(1)$^{\#3}$	1.930(6)	Na(1)-O(6)	2.464(3)
Li(1)-O(1)$^{\#4}$	1.930(6)	Na(1)-O(6)$^{\#5}$	2.464(3)
Li(1)-O(5)	1.944(7)	B(1)-O(1)	1.426(5)
Li(1)-O(5)$^{\#2}$	1.943(7)	B(1)-O(2)	1.494(5)
Na(1)-O(3)$^{\#2}$	2.907(3)	B(1)-O(3)	1.501(6)
Na(1)-O(3)$^{\#5}$	2.907(3)	B(1)-O(4)	1.468(5)
Na(1)-O(4)$^{\#5}$	2.895(3)	P(1)-O(2)$^{\#5}$	1.546(3)

Na(1)-O(4)$^{\#2}$	2.895(3)	P(1)-O(3)$^{\#3}$	1.545(3)
Na(1)-O(5)$^{\#6}$	2.461(4)	P(1)-O(4)	1.543(3)
Na(1)-O(5)	2.461(4)	P(1)-O(5)	1.497(3)
O(1)$^{\#4}$-Li(1)-O(1)$^{\#3}$	127.3(6)	O(5)-Na(1)-O(6)$^{\#5}$	138.42(11)
O(1)$^{\#3}$-Li(1)-O(5)	98.00(13)	O(5)$^{\#6}$-Na(1)-O(6)	138.42(11)
O(1)$^{\#4}$-Li(1)-O(5)	109.53(13)	O(6)-Na(1)-O(3)$^{\#5}$	76.43(9)
O(1)$^{\#3}$-Li(1)-O(5)$^{\#2}$	109.53(13)	O(6)-Na(1)-O(3)$^{\#2}$	81.17(9)
O(1)$^{\#4}$-Li(1)-O(5)$^{\#2}$	98.00(13)	O(6)$^{\#5}$-Na(1)-O(3)$^{\#5}$	81.17(9)
O(5)$^{\#2}$-Li(1)-O(5)	115.5(6)	O(6)$^{\#5}$-Na(1)-O(3)$^{\#2}$	76.43(9)
O(3)$^{\#5}$-Na(1)-O(3)$^{\#2}$	133.84(18)	O(6)$^{\#5}$-Na(1)-O(4)$^{\#5}$	70.01(8)
O(4)$^{\#5}$-Na(1)-O(3)$^{\#5}$	47.18(8)	O(6)-Na(1)-O(4)$^{\#5}$	121.84(7)
O(4)$^{\#5}$-Na(1)-O(3)$^{\#2}$	145.77(9)	O(6)-Na(1)-O(4)$^{\#2}$	70.01(8)
O(4)$^{\#2}$-Na(1)-O(3)$^{\#5}$	145.77(9)	O(6)$^{\#5}$-Na(1)-O(4)$^{\#2}$	121.84(7)
O(4)$^{\#2}$-Na(1)-O(3)$^{\#2}$	47.18(8)	O(6)$^{\#5}$-Na(1)-O(6)	120.7(3)
O(4)$^{\#2}$-Na(1)-O(4)$^{\#5}$	158.38(18)	O(1)-B(1)-O(2)	104.8(3)
O(5)-Na(1)-O(3)$^{\#5}$	78.38(9)	O(1)-B(1)-O(3)	114.4(4)
O(5)-Na(1)-O(3)$^{\#2}$	141.24(12)	O(1)-B(1)-O(4)	114.9(4)
O(5)$^{\#6}$-Na(1)-O(3)$^{\#2}$	78.38(9)	O(2)-B(1)-O(3)	108.1(3)
O(5)$^{\#6}$-Na(1)-O(3)$^{\#5}$	141.24(12)	O(4)-B(1)-O(2)	111.7(4)
O(5)$^{\#6}$-Na(1)-O(4)$^{\#2}$	69.50(9)	O(4)-B(1)-O(3)	102.9(3)
O(5)-Na(1)-O(4)$^{\#2}$	94.22(11)	O(3)$^{\#3}$-P(1)-O(2)$^{\#5}$	102.83(17)
O(5)-Na(1)-O(4)$^{\#}$5	69.50(9)	O(4)-P(1)-O(2)$^{\#5}$	110.11(17)
O(5)$^{\#6}$-Na(1)-O(4)$^{\#5}$	94.22(11)	O(4)-P(1)-O(3)$^{\#3}$	108.97(15)
O(5)-Na(1)-O(5)$^{\#6}$	84.95(18)	O(5)-P(1)-O(2)$^{\#5}$	112.49(15)
O(5)-Na(1)-O(6)	88.97(12)	O(5)-P(1)-O(3)$^{\#3}$	113.76(19)
O(5)$^{\#6}$-Na(1)-O(6)$^{\#5}$	88.97(12)	O(5)-P(1)-O(4)	108.54(16)

Symmetry transformations used to generate equivalent atoms:

#1 x, y, z-1 #2 -x+1, y, -z+1 #3 -x+1/2, y+1/2, -z

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

#7 x-1/2, y-1/2, z-1 #8 -x+1/2, y-1/2, -z

Table S4. Borophosphates with B:P = 1:1.

No	Compounds	Space group	FBB	Architectural feature	Dimensions	Ref.
1	$K_4B_2P_2O_9F_2$	$P2_1/c$	$[B_2P_2O_9F_2]$	4□: <3□>=<3□>	0D	[8]
2	$Mg(B(PO_4)(OH)_2)(H_2O)_2$	$R\bar{3}c$	$[BPO_5(OH)_2]$	6□: <6□>	0D	[9]
3	$KNi_5(P_6B_6O_{23}(OH)_{13})$	$Pa\bar{3}$	$[BPO_4(OH)_3]$	12□: <12□>	0D	[10]
4	$CaBPO_5$	$P3_121$	$[B_2P_2O_{12}]$	4□: <3□>□	1D	[11]
5	$SrBPO_5$	$P3_121$	$[B_2P_2O_{12}]$	4□: <3□>□	1D	[11]
6	$BaBPO_5$	$P3_121$	$[B_2P_2O_{12}]$	4□: <3□>□	1D	[12]
7	$PbBPO_5$	$P3_121$	$[B_2P_2O_{12}]$	4□: <3□>□	1D	[13]
8	$Al(B_2P_2O_7(OH)_5)(H_2O)$	$C2/c$	$[BPO_6(OH)]$	2□: 2□	1D	[14]
9	$Fe(B_2P_2O_7(OH)_5)$	$C2/c$	$[BPO_6(OH)]$	2□: 2□	1D	[15]
10	$Mg(BPO_4(OH)_2)$	$P3_121$	$[BPO_5(OH)_2]$	2□: 2□	1D	[16]
11	$Mg_3B_2(OH)_6(PO_4)_2(H_2O)_6$	$P\bar{1}$	$[BPO_4(OH)_3]$	2□: 2□	1D	[17]
12	$Ni(BPO_4(OH)_2)$	$P3_121$	$[BPO_5(OH)_2]$	2□: 2□	1D	[16]
13	$Co(BPO_4(OH)_2)$	$P3_121$	$[BPO_5(OH)_2]$	2□: 2□	1D	[18]
14	$Mn(BPO_4(OH)_2)$	$P3_121$	$[BPO_5(OH)_2]$	2□: 2□	1D	[18]
15	$Fe(BPO_4(OH)_2)$	$P3_121$	$[BPO_5(OH)_2]$	2□: 2□	1D	[18]
16	$ZnBPO_4(OH)_2$	$Pbcn$	$[BPO_5(OH)_2]$	2□: 2□	1D	[19]
17	$BaB_2P_2O_8F_2$	$P2_1/c$	$[B_2P_2O_{11}F_2]$	6□: <6□>	2D	[20]
18	$KBPO_4F$	Cc	$[BPO_6F]$	6□: <6□>	2D	[21]
19	$Cu(H_2O)_2(B_2P_2O_8(OH)_2)$	$Pbca$	$[BPO_6(OH)]$	6□: <6□>	2D	[22]
20	$Mg(H_2O)_2[B_2P_2O_8(OH)_2]\cdot H_2O$	$P2_1/c$	$[B_2P_2O_{10}(OH)_2]$	6□: <6□>	2D	[23]

21	$LiNaB_2P_2O_8(OH)_2 \cdot H_2O$	$C2$	$[BPO_6(OH)]$	6□: <6□>	2D	This work
22	$K_2B_2P_2O_9$	$P2_12_12_1$	$[B_2P_2O_{11}]$	4□: <3□>=<3□>	3D	[24]
23	$RbBPO_4F$	$P2_13$	$[BPO_6F]$	2□: 2□	3D	[25]
24	$CsBPO_4F$	$P2_13$	$[BPO_6F]$	2□: 2□	3D	[25]
25	NH_4BPO_4F	$P2_13$	$[BPO_6F]$	2□: 2□	3D	[26]
26	$RbB_2P_2O_8OH$	$P2_1/c$	$[B_2P_2O_{11}(OH)]$	4□: <3□>□	3D	[27]
27	$CsB_2P_2O_8OH$	$P2_1/c$	$[B_2P_2O_{11}(OH)]$	4□: <3□>□	3D	[27]
28	$LiNH_4B_2P_2O_9$	$P2_12_12_1$	$[B_2P_2O_{12}]$	4□: <3□>□	3D	This work
29	$LiKB_2P_2O_9$	$P2_12_12_1$	$[B_2P_2O_{12}]$	4□: <3□>□	3D	This work

□: tetrahedron; <…>: enclosed ring motifs; (–, =, ≡): the number of common polyhedron.

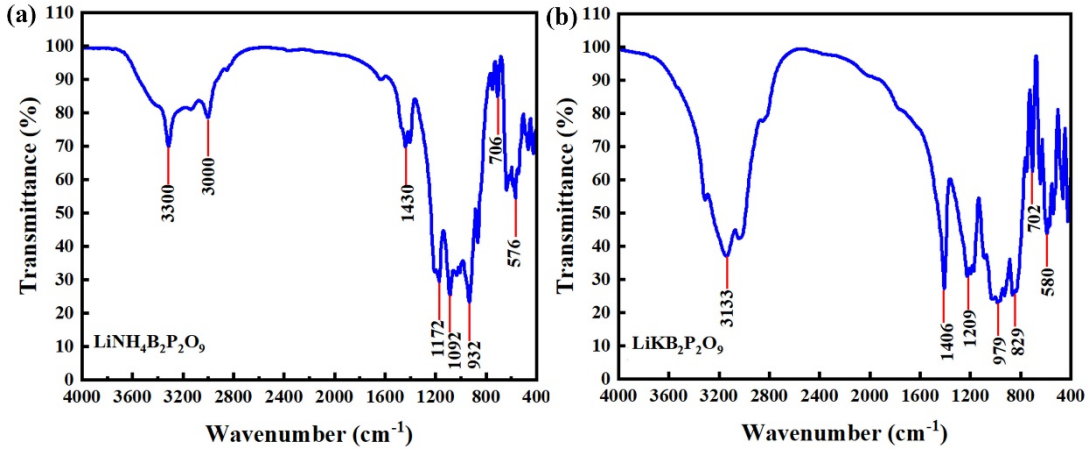

Figure S1. The IR of $LiAB_2P_2O_9$ (A = NH_4, K)

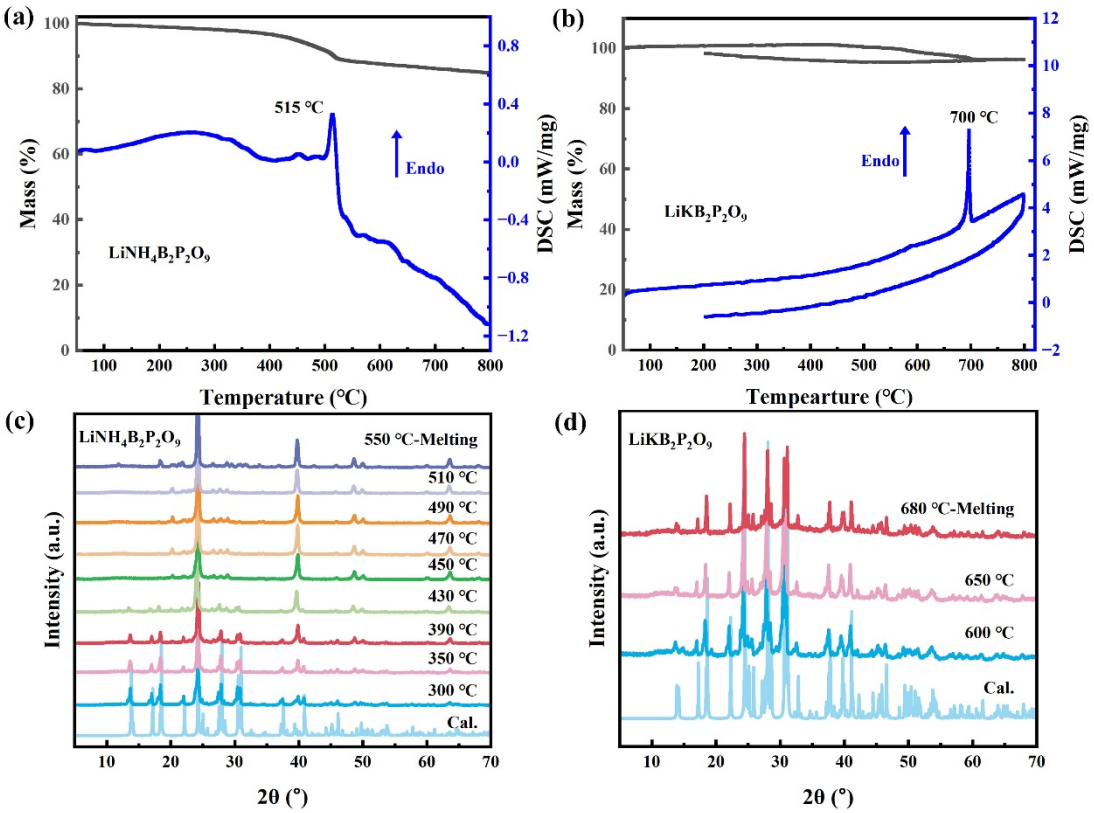

Figure S2. TG-DSC curves and calcinated XRD of $LiAB_2P_2O_9$ (A=NH_4, K).

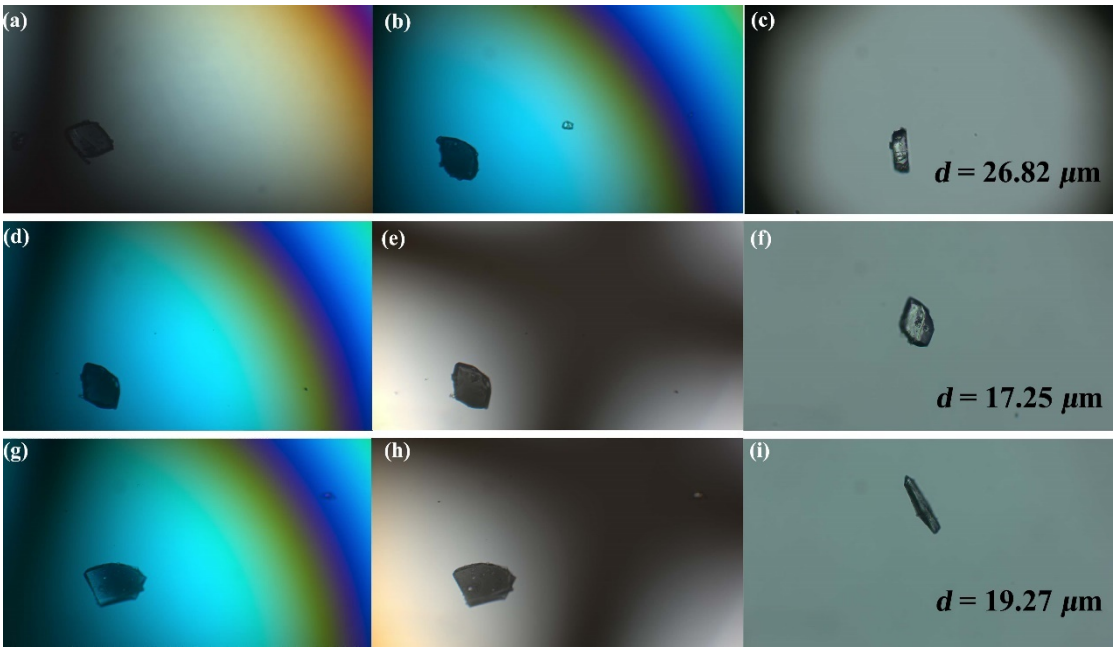

Figure S3. Birefringence measurement of $LiNH_4B_2P_2O_9$ (a-c), $LiKB_2P_2O_9$ (d-f), and $LiNaB_2P_2O_8(OH)_2 \cdot H_2O$ (g-i).

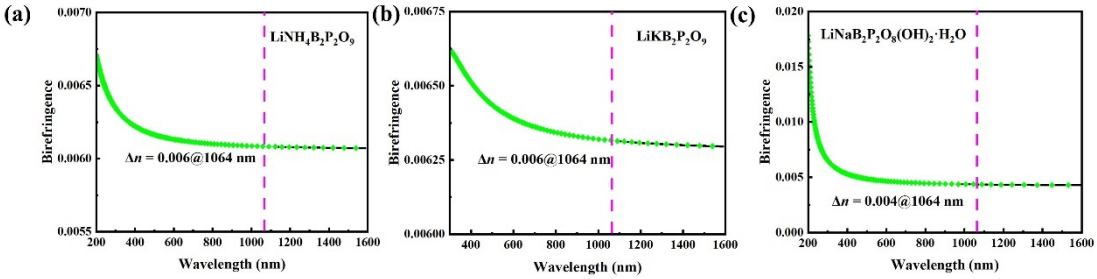

Figure S4. The calculated birefringence of $LiNH_4B_2P_2O_9$ (a), $LiKB_2P_2O_9$ (b), and $LiNaB_2P_2O_8(OH)_2 \cdot H_2O$ (c).

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