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$NH_4(B_6PO_{10}(OH)_4)\cdot H_2O$: Exhibiting the Largest Birefringence in Borophosphates

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CONTENTS

Experimetal Section:

Reagents

H_3BO_3 (Shanghai Aladdin Chemistry Co., Ltd., 99.5%), $NH_4H_2PO_4$ (Tianjin Fuchen Chemical Co., Ltd, 99.0%) and $SnCl_2·2H_2O$ (Shanghai Aladdin Chemistry Co., Ltd., 98.0%) were ground as received without further purification.

Synthesis

$NH_4(B_6PO_{10}(OH)_4)·H_2O$ crystals were synthesized by boric acid flux method. First, the mixtures containing H_3BO_3 (4mmol, 0.2473g), $NH_4H_2PO_4$ (1.15mmol, 0.1321g) and $SnCl_2·2H_2O$ (1mmol, 0.2257g) were put into a 23ml Teflon-lined stainless steel autoclave without any stirring and grinding. Then the Teflon-lined stainless steel autoclave was put into oven. The autoclave was heated to 220 °C within 3 h, held at that temperature for 3 days, and then cooled to 30 °C at a rate of 5 °C/h. Owing to the low yield (5% based on H_3BO_3), the final products were selected millimeter size crystals.

In addition, as is known that K, Rb, Cs-phases can often exhibit the similar structures with NH_4-phase, so we also had tried to synthesize the K, Rb, Cs-phases. But unfortunately, we did not succeed to obtain them.

Figure S1. The selected millimeter size crystals of $NH_4(B_6PO_{10}(OH)_4)\cdot H_2O$.

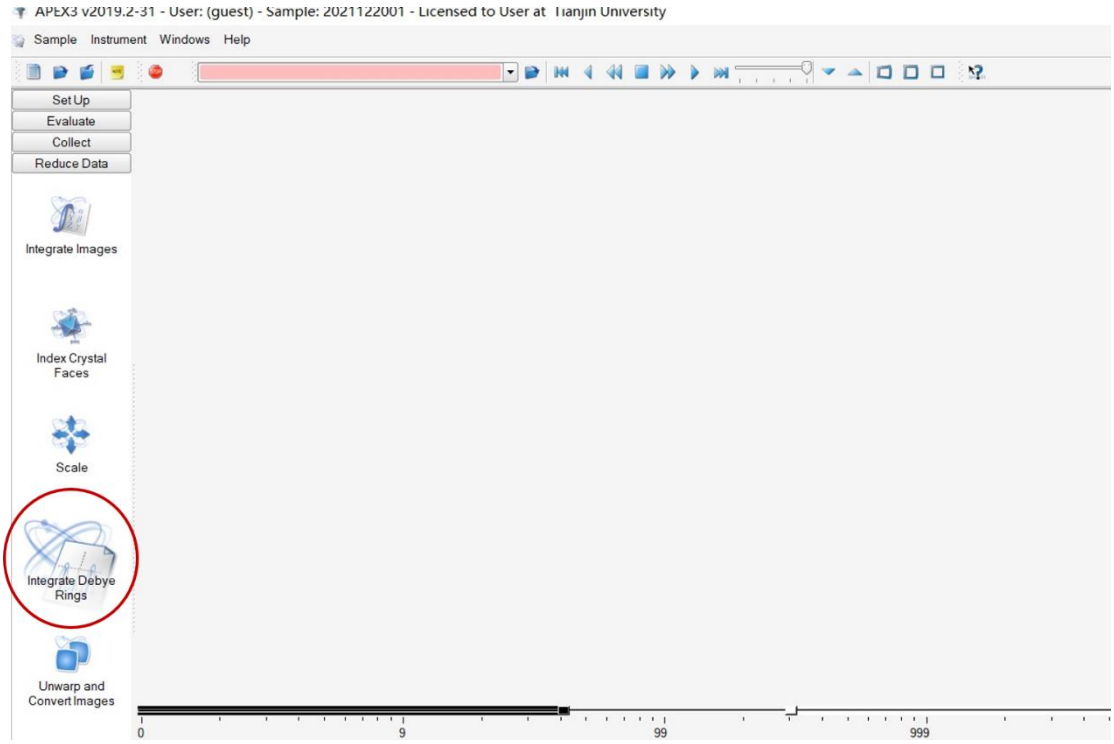

Figure S2. The program of X-ray powder diffraction patterns of $NH_4(B_6PO_{10}(OH)_4)\cdot H_2O$.

The powder X-ray diffraction data were collected using Bruker SMART APEX III CCD diffractometer with Integrate Debye Rings program at room temperature (Mo Kα radiation). Data were collected in the 2θ range of 10-70° with a step size of 2.00° and a step time of 60 s.

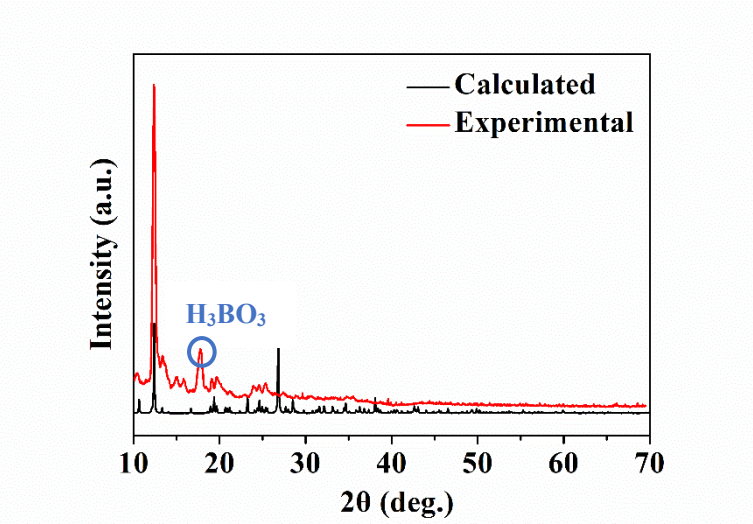

Figure S3. X-ray powder diffraction patterns of $NH_4(B_6PO_{10}(OH)_4)\cdot H_2O$.

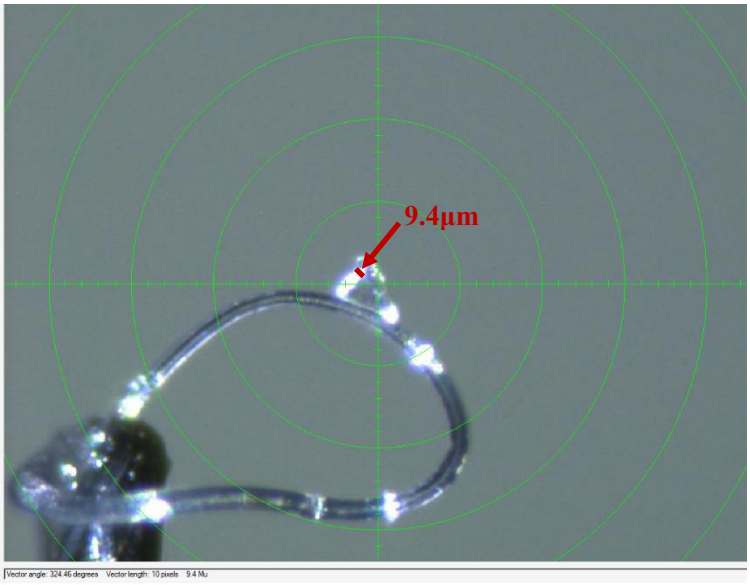

Figure S4. Photograph of crystal size.

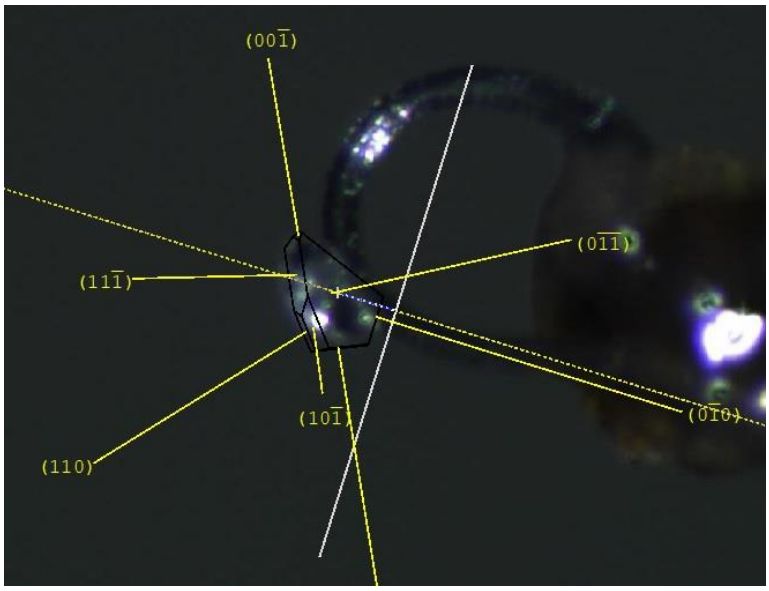

Figure S5. The crystal orientation of the $NH_4(B_6PO_{10}(OH)_4)\cdot H_2O$ was indexed by using a Bruker SMART APEX III.

Table S1. Atoms coordinates and equivalent isotropic displacement parameters for $NH_4(B_6PO_{10}(OH)_4)\cdot H_2O$.

Atoms	x	y	z	U(eq)	BVS
N(1)	1412(5)	6282(4)	8567(3)	40(1)	3.04
P(1)	2605(1)	4800(1)	5077(1)	16(1)	5.13
B(1)	2728(5)	9266(4)	2373(4)	22(1)	2.98
B(2)	-2203(5)	10025(4)	3752(4)	21(1)	2.98
B(3)	-966(5)	8342(5)	2080(4)	22(1)	2.98
B(4)	4297(5)	7748(5)	584(4)	25(1)	2.97
B(5)	-576(5)	7181(4)	4581(4)	16(1)	2.99
B(6)	4888(5)	6523(4)	3038(4)	19(1)	3.03
O(1)	1731(5)	4541(4)	1446(3)	63(1)	-2.51
O(2)	3681(3)	8052(2)	3358(2)	19(1)	-1.80
O(3)	-44(3)	7134(2)	3078(2)	19(1)	-1.80
O(4)	-1379(3)	8796(2)	4787(2)	19(1)	-1.83
O(5)	1024(3)	6331(2)	5337(2)	17(1)	-1.98
O(6)	-2133(3)	9781(3)	2434(2)	29(1)	-1.85
O(7)	2972(3)	9111(3)	989(2)	29(1)	-1.85
O(8)	5281(3)	6555(3)	1549(2)	20(1)	-1.87
O(9)	4116(3)	5179(2)	3851(2)	18(1)	-2.01
O(10)	1957(3)	3688(2)	4651(2)	19(1)	-1.98
O(11)	3315(3)	3944(3)	6501(2)	21(1)	-1.98
O(12)	1504(4)	10662(3)	2650(3)	32(1)	-1.05
O(13)	-731(4)	8186(3)	737(2)	34(1)	-1.03
O(14)	4614(4)	7629(3)	-785(3)	40(1)	-1.02
O(15)	-3109(4)	11548(3)	3902(3)	34(1)	-1.03

Table S2. Selected distances (Å) and angles (deg) for $NH_4(B_6PO_{10}(OH)_4)\cdot H_2O$.

N(1)-H(3)	0.8256	B(5)-O(4)	1.443(4)
N(1)-H(4)	0.8861	B(5)-O(3)	1.458(4)
N(1)-H(6)	0.9337	B(5)-O(5)	1.486(4)
N(1)-H(8)	0.7307	B(5)-O(10)#1	1.509(4)
O(1)-H(9)	0.8307	B(6)-O(8)	1.430(4)
O(1)-H(10)	0.7466	B(6)-O(2)	1.455(4)
B(1)-O(12)	1.349(5)	B(6)-O(11)#2	1.494(4)
B(1)-O(2)	1.363(4)	B(6)-O(9)	1.501(4)
B(1)-O(7)	1.392(5)	P(1)-O(9)	1.524(2)
B(2)-O(15)	1.353(4)	P(1)-O(10)	1.527(2)
B(2)-O(4)	1.356(4)	P(1)-O(11)	1.534(2)
B(2)-O(6)	1.393(5)	P(1)-O(5)	1.537(2)
B(3)-O(3)	1.357(4)	O(10)-B(5)#1	1.509(4)
B(3)-O(13)	1.353(5)	O(11)-B(6)#2	1.494(4)
B(3)-O(6)	1.395(4)	O(12)-H(7)	0.9840
B(4)-O(8)	1.355(4)	O(13)-H(2)	0.9543
B(4)-O(14)	1.357(5)	O(14)-H(1)	0.9128
B(4)-O(7)	1.397(5)	O(15)-H(5)	0.9603
H(3)-N(1)-H(4)	113.6	O(2)-B(6)-O(11)#2	109.9(3)
H(3)-N(1)-H(6)	122.7	O(8)-B(6)-O(9)	108.1(3)
H(4)-N(1)-H(6)	113.6	O(2)-B(6)-O(9)	111.7(3)
H(3)-N(1)-H(8)	112.8	O(11)#2-B(6)-O(9)	106.0(2)
H(4)-N(1)-H(8)	96.1	O(9)-P(1)-O(10)	105.45(13)
H(6)-N(1)-H(8)	92.5	O(9)-P(1)-O(11)	111.87(14)
O(12)-B(1)-O(2)	123.7(3)	O(8)-B(6)-O(11)#2	106.9(3)
O(12)-B(1)-O(7)	115.8(3)	O(2)-B(6)-O(11)#2	109.9(3)
O(2)-B(1)-O(7)	120.5(3)	O(8)-B(6)-O(9)	108.1(3)
O(15)-B(2)-O(4)	123.6(3)	O(2)-B(6)-O(9)	111.7(3)
O(15)-B(2)-O(6)	115.6(3)	O(11)#2-B(6)-O(9)	106.0(2)
O(4)-B(2)-O(6)	120.8(3)	O(9)-P(1)-O(10)	105.45(13)
O(3)-B(3)-O(13)	121.0(3)	O(9)-P(1)-O(11)	111.87(14)
O(3)-B(3)-O(6)	119.4(3)	O(8)-B(6)-O(11)#2	106.9(3)
O(13)-B(3)-O(6)	119.6(3)	O(2)-B(6)-O(11)#2	109.9(3)
O(8)-B(4)-O(14)	120.0(3)	O(8)-B(6)-O(9)	108.1(3)
O(8)-B(4)-O(7)	120.2(3)	O(2)-B(6)-O(9)	111.7(3)
O(14)-B(4)-O(7)	119.9(3)	O(11)#2-B(6)-O(9)	106.0(2)
O(4)-B(5)-O(3)	113.5(3)	O(9)-P(1)-O(10)	105.45(13)
O(4)-B(5)-O(5)	108.0(3)	O(9)-P(1)-O(11)	111.87(14)
O(3)-B(5)-O(5)	111.0(3)	O(8)-B(6)-O(11)#2	106.9(3)
O(4)-B(5)-O(10)#1	107.4(3)	O(2)-B(6)-O(11)#2	109.9(3)
O(3)-B(5)-O(10)#1	110.6(3)	O(5)-B(5)-O(10)#1	106.0(3)
O(8)-B(6)-O(11)#2	106.9(3)	O(8)-B(6)-O(2)	113.8(3)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1 #2 -x+1,-y+1,-z+1

Table S3. Hydrogen bonds for $NH_4(B_6PO_{10}(OH)_4)\cdot H_2O$.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(10)...O(10)	0.75	2.51	3.087(4)	135.8
O(1)-H(10)...O(3)	0.75	2.38	3.019(4)	145.1
O(1)-H(9)...O(14)#3	0.83	2.14	2.886(4)	148.9
N(1)-H(8)...O(15)#4	0.73	2.28	3.003(4)	169.3
O(12)-H(7)...O(4)#4	0.98	1.76	2.741(4)	177.7
O(15)-H(5)...O(2)#4	0.96	1.82	2.778(4)	174.7
N(1)-H(4)...O(8)#2	0.89	2.07	2.936(4)	164.6
N(1)-H(3)...O(13)#5	0.83	2.18	2.982(4)	163.9
O(13)-H(2)...O(12)#6	0.95	2.63	3.367(4)	133.8
O(13)-H(2)...O(7)#6	0.95	1.88	2.816(3)	167.0
O(14)-H(1)...O(6)#6	0.91	1.93	2.829(4)	166.4

Symmetry transformations used to generate equivalent atoms:

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

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

Table S4. A summary of mixed-coordinated borophosphates.

BPOs	**Synthesis**	**B:P**	**BO_3:BO_4**
$M_2[BP_3O_{12}]$(M=Cr,V,Fe)	Solid state	1:3	3:0
$Co_5[BPO_6][PO_4]_2$	Low temperature flux	1:3	1:0
$CsSc[B_2P_3O_{11}(OH)_2]$	Hydrothermal	2:3	1:1
$[C_6H_{14}N_2]_2[VOB_3P_4O_{15}(OH)_5]\cdot H_2O$	Hydrothermal	3:4	1:2
$Na_2[MB_3P_2O_{11}(OH)]\cdot 0.67H_2O$(M=Co,Fe,Mn,Ni,Zn)	Low temperature flux	3:2	1:2
$Na_5(H_3O)\{M_3[B_3O_3(OH)]_3(PO_4)_6\}\cdot 2H_2O$ (M=Mn,Co,Ni)	Hydrothermal	3:2	1:2
$Na_5(NH_4)Mn_3[B_9P_6O_{33}(OH)_3]\cdot 1.5H_2O$	Hydrothermal	3:2	1:2
$Na_8[Cr_4B_{12}P_8O_{44}(OH)_4][P_2O_7]\cdot nH_2O$	Hydrothermal	3:2	1:2
$Na_2[VB_3P_2O_{12}(OH)]\cdot 2.92H_2O$	Low temperature flux	3:2	1:2
$Na_5KCu_3[B_9P_2O_{33}(OH)_3]\cdot H_2O$	Low temperature flux	3:2	1:2
$LiNa_2B_5P_2O_{14}$	Solid state	5:2	2:3
$Li_2B_3PO_8$	Solid state	3:1	2:1
$Li[B_3PO_6(OH)_3]$	Hydrothermal	3:1	2:1
$(NH_4)_2[B_3PO_7(OH)_2]$	Hydrothermal	3:1	2:1
$(NH_4)[B_3PO_6(OH)_3]\cdot 0.5H_2O$	Solvothermal	3:1	2:1
$K_2MB_4PO_{10}$(M=Rb,Cs)	Solid state	4:1	2:2
$K_3B_4PO_{10}$	Solid state	4:1	2:2
$K_3[B_5PO_{10}(OH)_3]$	Hydrothermal	5:1	2:3
$Na_3B_6PO_{13}$	Solid state	6:1	4:2
$K[B_6PO_{10}(OH)_4]$	Hydrothermal	6:1	4:2