Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Hexameric poly-fluoroberyllophosphate $Na_4Be_2PO_4F_5$ with moderate birefringence and deep-ultraviolet transmission as potential zero-order-waveplate crystal

Yuanyu Yang,[a] Yao Guo,[b] Yi-Gang Chen,*[a] Xiwei Hu,[a] Xia Zhang,[a] Xian-Ming Zhang,*[a,c]

[a] *Key Laboratory of Magnetic Molecules and Magnetic Information of Ministry of Education, School of Chemistry and Material Science, Shanxi Normal University, Taiyuan 030006, China.*

[b] *Henan Joint International Research Laboratory of Nanocomposite Sensing Materials, School of Materials Science and Engineering, Anyang Institute of Technology, Anyang 455000, China.*

[c] *College of Chemistry & Chemical Engineering, Key Laboratory of Interface Science and Engineering in Advanced Material, Ministry of Education, Taiyuan University of Technology, Yingze West, Taiyuan 030024, China.*

Table of Contents

Table S1. Selected bond distances (Å) and angles (deg) for (a)$Na_4Be_2PO_4F_5$ and (b) $KBe[PO_3(OH)]F$.

(a)

Be(1)−O(3)	1.6120 (15)	Na(2)−F(5)	2.2622 (8)
Be(1)−F(1l)	1.5519 (15)	Na(3)−O(3b)	2.4561 (9)
Be(1)−F(2)	1.5339 (15)	Na(3)−O(4j)	2.2726 (9)
Be(1)−F(5c)	1.5719 (15)	Na(3)−F(1h)	2.4350 (8)
Be(2)−O(1)	1.6096 (15)	Na(3)−F(1)	2.2682 (8)
Be(2)−O(2)	1.6506 (15)	Na(3)−F(3)	2.3838 (10)
Be(2)−F(3c)	1.5464 (15)	Na(3)−F(4i)	2.4604 (11)
Be(2)−F(4)	1.5596 (15)	Na(4)−O(2k)	2.3886 (10)
P(1)−O(1c)	1.5361 (9)	Na(4)−O(3)	2.4698 (12)
P(1)−O(2)	1.5500 (8)	Na(4)−F(1c)	2.5749 (9)
P(1)−O(3)	1.5452 (8)	Na(4)−F(3c)	2.2281 (8)
P(1)−O(4)	1.5079 (8)	Na(4)−F(4k)	2.6931 (8)
Na(1)−O(4b)	2.3578 (9)	Na(4)−F(5l)	2.2706 (8)
Na(1)−O(4d)	2.3578 (9)	Na(4)−F(5c)	2.6444 (9)
Na(1)−F(2e)	2.3101 (7)	Na(5)−O(2f)	2.5881 (10)
Na(1)−F(2)	2.3101 (7)	Na(5)−O(2d)	2.5881 (10)
Na(1)−F(4f)	2.3048 (7)	Na(5)−F(2)	2.3606 (8)
Na(1)−F(4g)	2.3048 (7)	Na(5)−F(2c)	2.3606 (8)
Na(2)−O(1c)	2.3789 (9)	Na(5)−F(4d)	2.6557 (10)
Na(2)−O(4b)	2.3418 (10)	Na(5)−F(4f)	2.6557 (10)

Na(2)−F(1)	2.7835 (11)	Na(5)−F(5c)	2.4787 (9)
Na(2)−F(2)	2.2564 (10)	Na(5)−F(5)	2.4787 (9)
Na(2)−F(3)	2.3517 (8)		
O(3)−Be(1)−F(1l)	104.80 (8)	O(4b)−Na(2)−F(1)	76.18 (3)
O(1)−Be(2)−O(2)	113.10 (9)	O(4j)−Na(3)−O(3b)	144.39 (3)
O(1)−Be(2)−F(3c)	104.57 (9)	O(3b)−Na(3)−F(4i)	92.18 (3)
O(1)−Be(2)−F(4)	115.89 (9)	O(2k)−Na(4)−O(3)	125.38 (4)
O(1c)−P(1)−O(3)	108.69 (4)	O(2k)−Na(4)−F(1c)	102.76 (3)
O(3)−P(1)−O(2)	108.65 (5)	O(2f)−Na(5)−O(2d)	81.11 (4)
O(4d)−Na(1)−O(4b)	180.0	O(2d)−Na(5)−F(4f)	91.31 (3)

Symmetry transformations used to generate equivalent atoms:

(a) *x*, *y*-1, *z*; (b) -*x*+1, -*y*+2, -*z*+1; (c) -*x*+1, *y*, -*z*+1/2; (d) *x*, *y*+1, *z*; (e) -*x*+1, -*y*+3, -*z*+1; (f) -*x*+1, *y*+1, -*z*+1/2; (g) *x*, -*y*+2, *z*+1/2; (h) -*x*+3/2, *y*-1/2, -*z*+3/2; (i) *x*+1/2, *y*+1/2, *z*+1; (j) *x*+1/2, -*y*+3/2, *z*+1/2; (k) -*x*+1/2, -*y*+3/2, -*z*; (l) *x*-1/2, -*y*+5/2, *z*-1/2; (m) -*x*+1/2, -*y*+5/2, -*z*; (n) -*x*+3/2, *y*+1/2, -*z*+3/2; (o) *x*+1/2, -*y*+5/2, *z*+1/2; (p) -*x*+1, *y*-1, -*z*+1/2; (q) *x*-1/2, *y*-1/2, *z*-1; (r) *x*-1/2, -*y*+3/2, *z*-1/2.

(b)

Be(1)−O(7)	1.634 (2)	K(1)−O(1c)	2.7364 (13)
Be(1)−O(6)	1.626 (2)	K(1)−O(2)	2.7642 (13)
Be(1)−O(3)	1.626 (2)	K(1)−O(3e)	2.9253 (12)
Be(1)−F(2)	1.541 (2)	K(1)−O(5b)	2.7591 (12)
P(1)−O(1)	1.5745 (13)	K(1)−O(6d)	2.9663 (13)
P(1)−O(3h)	1.5280 (13)	K(1)−O(8b)	2.8648 (12)
P(1)−O(6g)	1.5177 (11)	K(1)−F(1c)	2.6268 (10)

P(1)−O(8)	1.5174 (12)	K(1)−F(2)	2.7921 (11)
Be(2h)−O(4)	1.633 (2)	K(2)−O(1a)	2.9518 (14)
Be(2)−O(5)	1.632 (2)	K(2)−O(2e)	2.8552 (13)
Be(2)−O(8)	1.638 (2)	K(2)−O(3e)	3.0155 (12)
Be(2)−F(1)	1.529 (2)	K(2)−O(5)	3.1588 (13)
P(2)−O(2)	1.5734 (13)	K(2)−O(6c)	3.2165 (12)
P(2)−O(4)	1.5314 (13)	K(2)−O(7c)	2.7851 (12)
P(2)−O(5)	1.5138 (11)	K(2)−O(8)	3.3385 (12)
P(2)−O(7)	1.5098 (11)	K(2)−F(1c)	2.7633 (11)
O(1)−H(1)	0.68 (2)	K(2)−F(1)	2.7476 (11)
O(2)−H(2)	0.82 (3)	K(2)−F(2c)	3.4069 (11)
O(3)−Be(1)−O(7)	111.38 (14)	O(4h)−Be(2)−O(8)	111.27 (14)
O(3)−Be(1)−F(2)	109.56 (14)	O(8)−Be(2)−F(1)	111.15 (14)
O(3h)−P(1)−O(1)	105.93 (7)	O(4)−P(2)−O(2)	106.22 (7)
O(6g)−P(1)−O(1)	107.73 (7)	O(1a)−K(2)−O(3e)	49.03 (3)
O(1c)−K(1)−O(2)	150.53 (4)	O(1a)−K(2)−O(5)	129.50 (3)
O(1c)−K(1)−O(5b)	84.37 (4)	O(1a)−K(2)−F(2c)	115.31 (3)
O(2)−K(1)−F(2)	71.93 (3)	O(2e)−K(2)−F(2c)	99.99 (3)
O(5b)−K(1)−F(2)	70.04 (3)	O(3e)−K(2)−F(2c)	157.41 (3)

Symmetry codes: (a) *x*+1/2, -*y*+1/2, *z*-1/2; (b) -*x*+1/2, *y*+1/2, -*z*+1/2; (c) -*x*+1, -*y*+1, -*z*+1; (d) *x*+1/2, -*y*+3/2, *z*-1/2; (e) -*x*+1/2, *y*-1/2, -*z*+1/2; (f) *x*-1/2, -*y*+1/2, *z*+1/2; (g) *x*, *y*-1, *z*; (h) -*x*, -*y*+1, -*z*+1; (i) *x*-1/2, -*y*+3/2, *z*+1/2; (j) *x*, *y*+1, *z*.

Table S2. Atomic coordinates，equivalent isotropic displacement parameters ($Å^2$) for (a) $Na_4Be_2PO_4F_5$ and (b) $KBe[PO_3(OH)]F$. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(a)

Atom	Wyck.	Site	x/a	y/b	z/c	BVS
P1	8f	1	0.40923(2)	0.82091(3)	0.27680(2)	5.00
Be1	8f	1	0.36665(9)	1.20614(18)	0.22229(13)	1.98
Be2	8f	1	0.39721(9)	0.76191(18)	0.05890(13)	1.98
Na1	4a	-1	1/2	1.50000	1/2	1.16
Na2	8f	1	0.59347(3)	1.14243(6)	0.49146(4)	1.06
Na3	8f	1	0.77023(3)	0.96832(6)	0.77727(4)	1.05
Na4	8f	1	0.23233(3)	1.00435(6)	-0.02314(4)	1.02
Na5	4e	2	1/2	1.44808(9)	1/4	0.94
O1	8f	1	0.48885(5)	0.87466(10)	0.12516(7)	1.97
O2	8f	1	0.38671(5)	0.71226(11)	0.16311(7)	1.98
O3	8f	1	0.35017(5)	0.99343(10)	0.21939(8)	2.04
O4	8f	1	0.38760(5)	0.71072(11)	0.34321(7)	1.98
F1	8f	1	0.78190(4)	1.20409(9)	0.68668(7)	0.98
F2	8f	1	0.45753(4)	1.28672(9)	0.34678(6)	1.04
F3	8f	1	0.68233(4)	0.88235(9)	0.55471(6)	1.02
F4	8f	1	0.39072(4)	0.57208(9)	0.00581(6)	0.96
F5	8f	1	0.63796(5)	1.25309(9)	0.39172(6)	1.04

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P1	0.00859(13)	0.00772(13)	0.00897(13)	0.00029(8)	0.00626(11)	0.00011(8)
Be1	0.0132(6)	0.0105(6)	0.0130(6)	0.0002(4)	0.0092(5)	-0.0003(4)
Be2	0.0107(5)	0.0113(6)	0.0124(6)	0.0002(4)	0.0082(5)	-0.0001(4)
Na1	0.0152(3)	0.0147(3)	0.0149(3)	0.0024(2)	0.0108(2)	0.0016(2)
Na2	0.0219(2)	0.0173(2)	0.0177(2)	0.00361(17)	0.0144(2)	0.00074(17)
Na3	0.0168(2)	0.0183(2)	0.0192(2)	0.00239(16)	0.01320(19)	0.00354(17)
Na4	0.0161(2)	0.0191(2)	0.0192(2)	0.00063(17)	0.0102(2)	-0.00178(17)
Na5	0.0208(3)	0.0166(3)	0.0265(3)	0.00000	0.0174(3)	0.00000
O1	0.0102(3)	0.0141(4)	0.0147(4)	0.0001(3)	0.0078(3)	0.0024(3)
O2	0.0170(4)	0.0162(4)	0.0144(3)	-0.0049(3)	0.0125(3)	-0.0047(3)
O3	0.0114(3)	0.0094(4)	0.0199(4)	0.0015(3)	0.0086(3)	0.0018(3)
O4	0.0163(4)	0.0156(4)	0.0142(4)	-0.0010(3)	0.0118(3)	0.0017(3)
F1	0.0186(3)	0.0151(3)	0.0236(3)	-0.0048(2)	0.0158(3)	-0.0022(2)
F2	0.0158(3)	0.0159(3)	0.0154(3)	-0.0028(2)	0.0077(3)	-0.0037(2)
F3	0.0118(3)	0.0181(3)	0.0146(3)	-0.0034(2)	0.0066(3)	-0.0035(2)
F4	0.0232(3)	0.0138(3)	0.0216(3)	-0.0011(2)	0.0175(3)	-0.0039(2)
F5	0.0234(3)	0.0205(3)	0.0186(3)	-0.0034(3)	0.0169(3)	-0.0033(3)

(b)

Atom	Wyck.	Site	x/a	y/b	z/c	BVS
P1	4e	1	0.16300(5)	0.08053(4)	0.60944(4)	5.01
P2	4e	1	0.10578(5)	0.57972(4)	0.37624(4)	5.04
Be1	4e	1	0.1815(3)	0.8614(2)	0.43811(19)	2.03
Be2	4e	1	0.2115(3)	0.3638(2)	0.54256(19)	2.02
K1	4e	1	0.47035(5)	0.70855(4)	0.21330(3)	1.03
K2	4e	1	0.52610(5)	0.31339(5)	0.39494(4)	0.89
F1	4e	1	0.38493(12)	0.40709(10)	0.59238(9)	0.96
F2	4e	1	0.33227(13)	0.89187(11)	0.36955(9)	0.74
O1	4e	1	0.27211(16)	0.11254(13)	0.72939(11)	2.13
O2	4e	1	0.15963(16)	0.61113(13)	0.24831(11)	2.16
O3	4e	1	0.01535(14)	0.91488(12)	0.35996(10)	2.01
O4	4e	1	-0.08263(14)	0.58385(12)	0.36413(10)	1.78
O5	4e	1	0.16891(15)	0.43485(11)	0.41129(10)	2.06
O6	4e	1	0.20649(15)	0.93443(11)	0.56919(10)	2.02
O7	4e	1	0.17771(14)	0.69220(11)	0.46006(10)	2.01
O8	4e	1	0.19944(15)	0.19409(12)	0.52125(10)	1.98
H1	4e	1	0.298(3)	0.052(2)	0.757(2)	0.89
H2	4e	1	0.150(4)	0.539(3)	0.208(3)	0.78

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K1	0.0172(2)	0.01511(19)	0.0189(2)	0.00067(15)	-0.00182(15)	0.00036(15)
P1	0.0125(2)	0.00720(19)	0.0095(2)	0.00022(16)	-0.00092(16)	0.00033(16)
K2	0.0232(2)	0.0314(2)	0.0229(2)	-0.00468(19)	0.00110(17)	-0.00498(18)
P2	0.0119(2)	0.00711(19)	0.0088(2)	-0.00006(16)	0.00080(16)	0.00007(16)
F1	0.0133(5)	0.0200(5)	0.0199(5)	-0.0014(4)	-0.0024(4)	0.0006(4)
F2	0.0185(5)	0.0199(5)	0.0235(5)	0.0011(4)	0.0086(4)	0.0040(4)
O8	0.0204(7)	0.0095(6)	0.0124(6)	0.0012(5)	0.0013(5)	0.0012(5)
O7	0.0168(6)	0.0090(5)	0.0143(6)	-0.0004(5)	-0.0026(5)	-0.0008(5)
O6	0.0227(7)	0.0087(5)	0.0119(6)	0.0021(5)	-0.0019(5)	-0.0004(5)
O5	0.0245(7)	0.0077(5)	0.0117(6)	0.0016(5)	-0.0002(5)	0.0008(5)
O4	0.0117(6)	0.0165(6)	0.0158(6)	-0.0008(5)	0.0008(5)	-0.0054(5)
O2	0.0215(7)	0.0124(6)	0.0126(6)	0.0006(5)	0.0057(5)	0.0017(5)
O1	0.0192(7)	0.0107(6)	0.0136(6)	-0.0003(5)	-0.0059(5)	0.0017(5)
O3	0.0136(6)	0.0159(6)	0.0162(6)	0.0012(5)	0.0003(5)	0.0035(5)
Be1	0.0158(11)	0.0097(10)	0.0099(10)	-0.0006(8)	-0.0001(8)	-0.0001(8)
Be2	0.0143(11)	0.0094(10)	0.0114(10)	0.0001(8)	-0.0005(8)	0.0004(8)

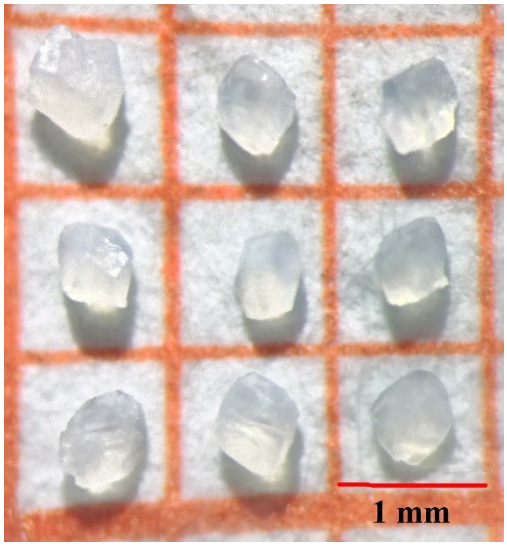
Table S3. Energy-Dispersive Spectrometry (EDS) for $Na_4Be_2PO_4F_5$ and $KBe[PO_3(OH)]F$.

(a)

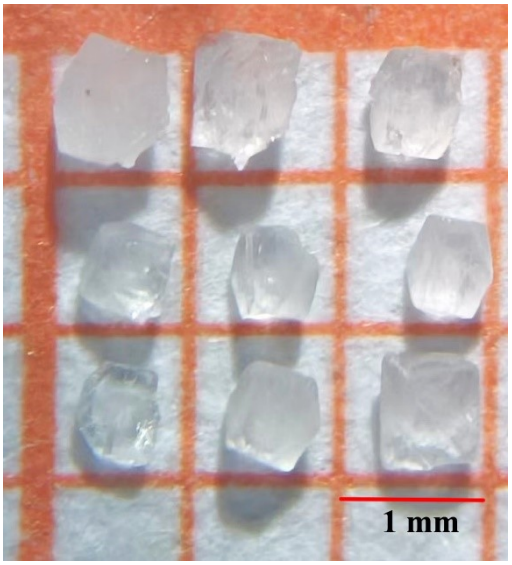
Point 1				Point 2			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
O K	23.10	28.95		O K	24.02	30.08	
F K	36.90	34.96	5.27	F K	33.87	35.72	4.95
Na M	31.15	27.17	4.45	Na M	30.96	26.98	3.74
P M	6.98	10.78	1	P M	11.15	7.21	1
Totals	100.00			Totals	100.00		
Point 3							
Element	Weight%	Atomic%	Formula				
O K	28.95	35.72		The average Na:P:F molar ratio: 4.16:1:5.08			
F K	30.13	31.30	5.02				
Na M	31.15	26.75	4.29				
P M	9.77	6.23	1				
Totals	100.00						

(b)

Point 1				Point 2			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
O K	3.41	54.37		O K	43.02	58.29	
F K	4.94	15.93	1.15	F K	11.81	13.47	1.04
KK	1.79	13.80	1	KK	23.23	12.88	1
P K	1.65	15.90	1.15	P K	21.93	15.35	1.19
Totals	100.00			Totals	100.00		
Point 3							
Element	Weight%	Atomic%	Formula				
O K	57.13	69.78		The average K:P:F molar ratio: 1:1.15:1.09			
F K	10.23	10.29	1.08				
KK	19.52	9.46	1				
P K	15.28	10.47	1.11				
Totals	100.00						



(a)



(b)

Figure S1. Photos of the crystals (a) $Na_4Be_2PO_4F_5$ and (b) $KBe[PO_3(OH)]F$.

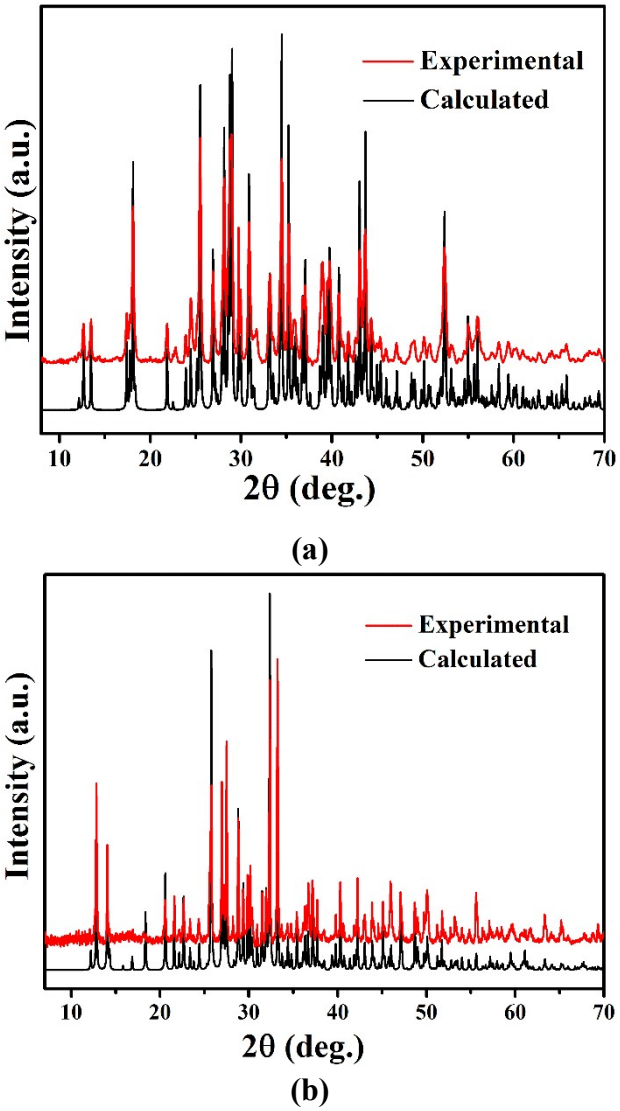


Figure S2. Powder XRD patterns for (a) $Na_4Be_2PO_4F_5$ and (b) $KBe[PO_3(OH)]F$.

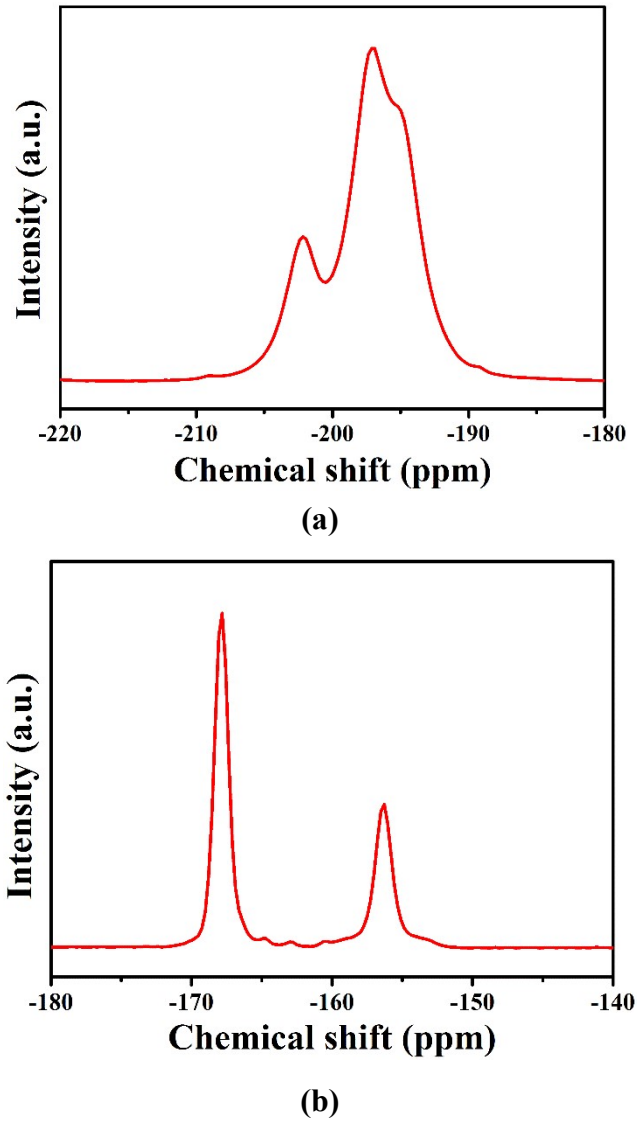
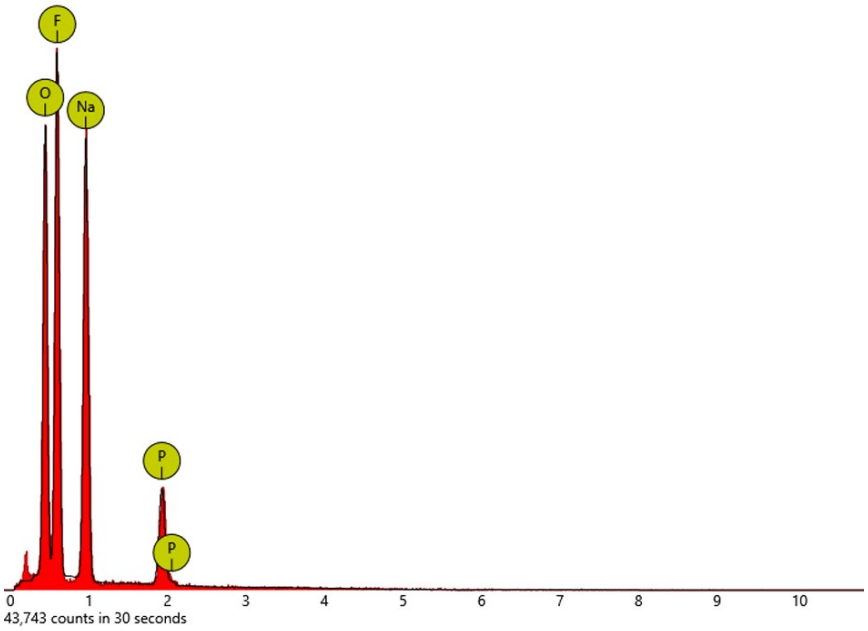
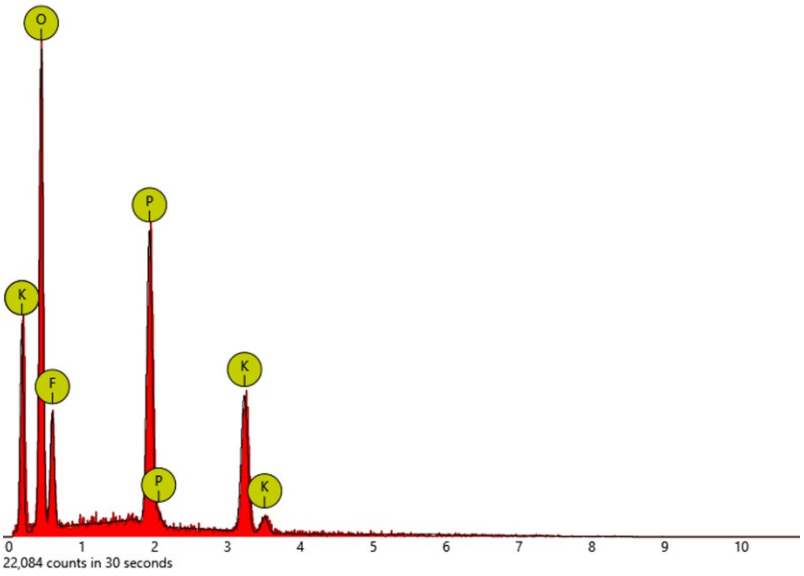


Figure S3. ^{19}F MAS NMR spectra of (a) $Na_4Be_2PO_4F_5$ and (b) $KBe[PO_3(OH)]F$.



(a)



(b)

Figure S4. Energy-Dispersive Spectrometry (EDS) for (a) $Na_4Be_2PO_4F_5$ and (b) $KBe[PO_3(OH)]F$.

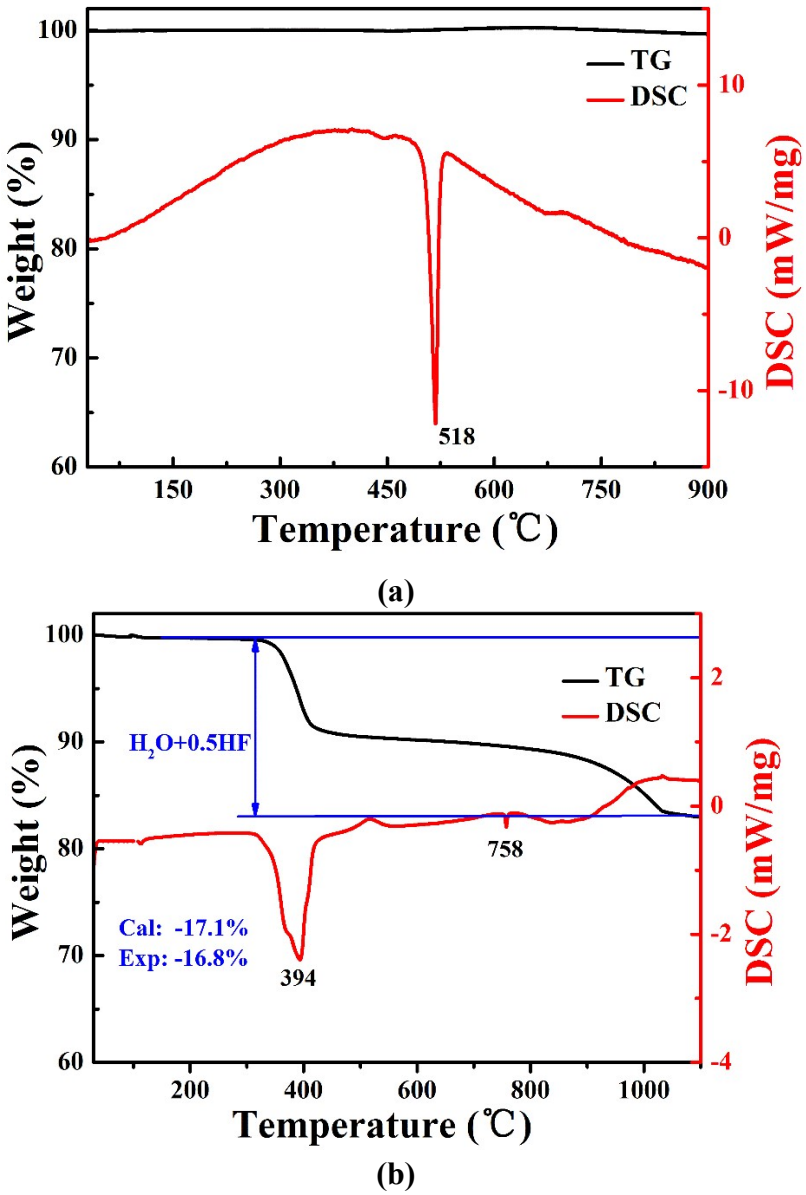


Figure S5. TG and DSC curves for (a) $Na_4Be_2PO_4F_5$ and (b) $KBe[PO_3(OH)]F$.

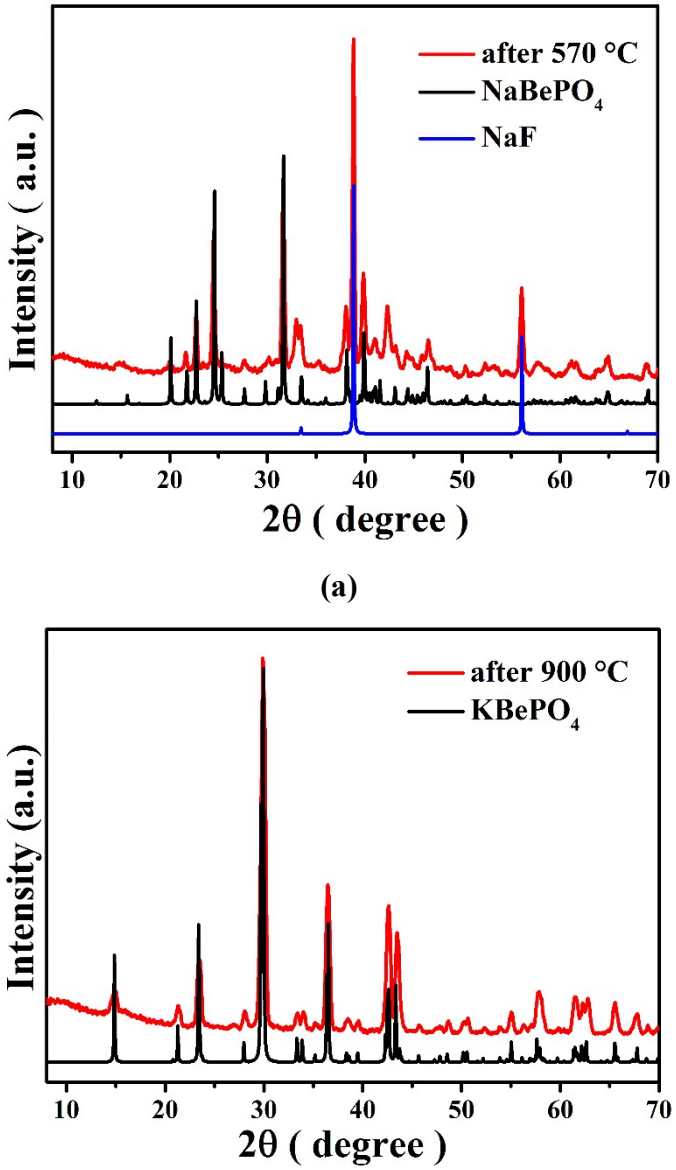


Figure S6. XRD patterns for (a) $Na_4Be_2PO_4F_5$ after 570 °C and (b) $KBe[PO_3(OH)]F$ after 900 °C.

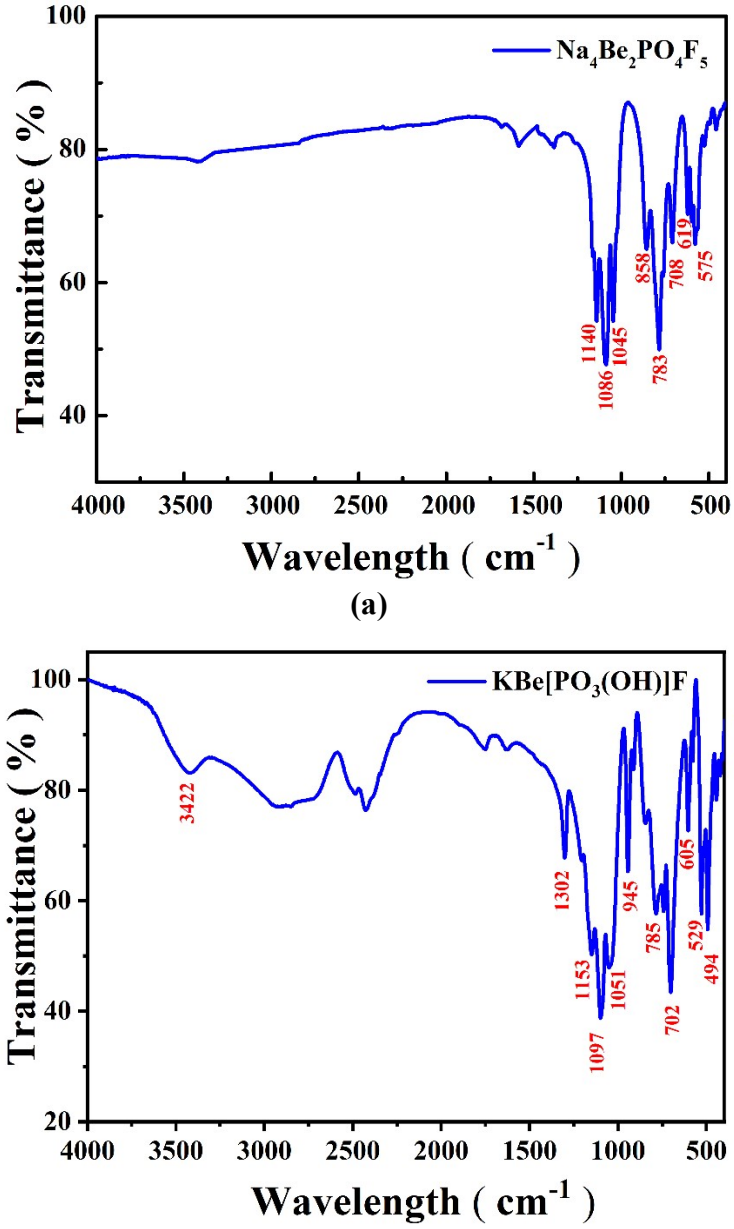
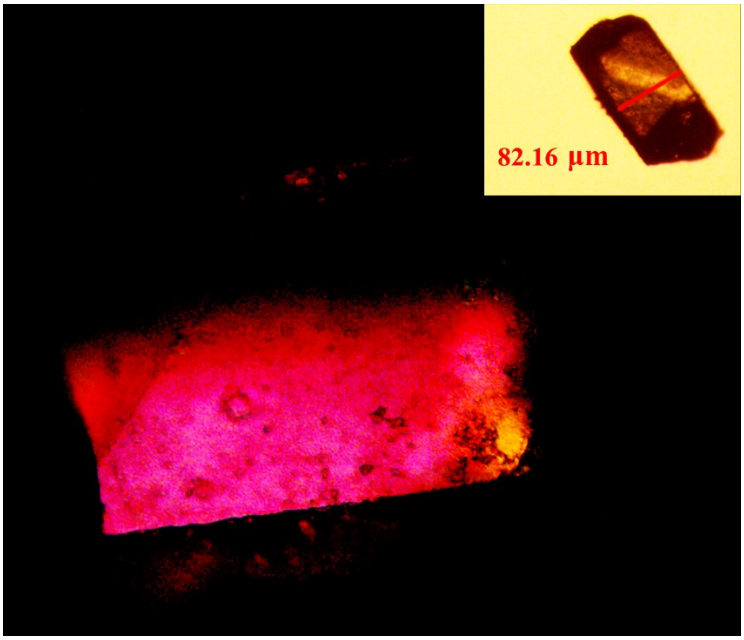
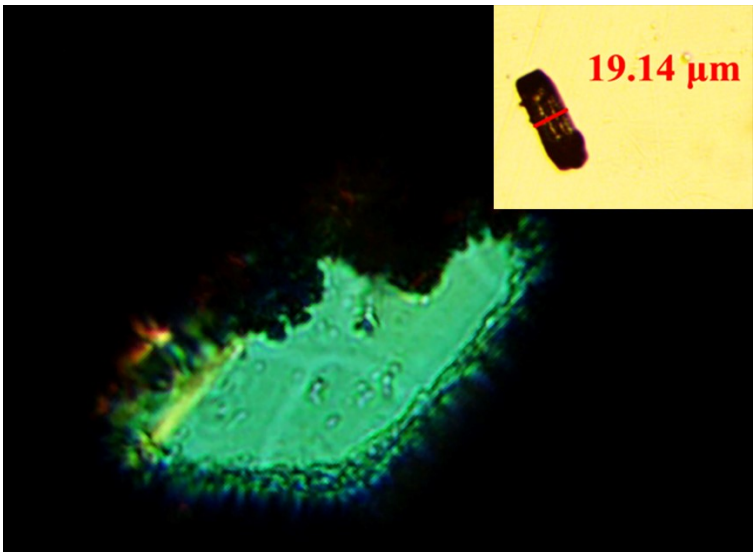


Figure S7. IR spectra of (a) $Na_4Be_2PO_4F_5$ and (b) $KBe[PO_3(OH)]F$.



(a)



(b)

Figure S8. Birefringence measurements of $Na_4Be_2PO_4F_5$ (a) and $KBe[PO_3(OH)]F$(b) crystal under a cross-polarizing microscope. $Na_4Be_2PO_4F_5$ and $KBe[PO_3(OH)]F$ have the thicknesses of 82.16 and 19.14 μm, respectively. Optical path differences of two tested crystal are about 540 and 710 nm, with the first-order pink and second-order green, respectively, according to Michal–Levy diagram.