Two New Ammonium/Alkali-Rare Earth Metal Difluorophosphate $ALa(PO_2F_2)_4$ (A = NH_4 and K;) with Moderate Birefringence and Short Cut-off Edges

Wenyao Zhang,[a, b] Zhonglei Wei,[a,b] Zhihua Yang,[a] Shilie Pan*[a]

[a]CAS Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics & Chemistry, CAS, and Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40-1 South Beijing Road, Urumqi 830011, China

[b]Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

*To whom correspondence should be addressed. Phone: (+86)991-3674558.
Fax: (+86)991-3838957. E-mail: slpan@ms.xjb.ac.cn (S. Pan).

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS for $KLa(PO_2F_2)_4$. U_{eq} is defined as one-third of the trace of the orthogonalizedU_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
K(1)	3534(1)	1512(1)	4407(1)	33(1)	0.95
La(1)	7182(1)	5836(1)	5096(1)	16(1)	3.21
P(1)	3802(1)	5491(1)	1983(1)	22(1)	4.98
P(2)	5878(1)	3449(1)	4118(1)	24(1)	5.06
P(3)	10784(1)	5164(1)	7248(1)	24(1)	5.06
P(4)	8699(1)	7725(1)	3532(1)	26(1)	5.11
O(1)	5152(3)	5888(2)	2704(3)	27(1)	1.98
O(2)	4602(3)	3134(2)	4381(3)	27(1)	2.04
O(3)	3371(3)	4674(2)	2527(3)	28(1)	1.86
O(4)	9354(3)	5120(2)	6306(3)	32(1)	2.01
O(5)	7587(3)	7210(2)	3822(3)	32(1)	2.07
O(6)	11826(3)	4549(2)	7035(3)	28(1)	1.98
O(7)	6383(3)	4317(2)	4651(3)	32(1)	1.96
O(8)	8485(3)	8104(2)	2034(3)	32(1)	1.99
F(1)	3720(3)	5363(2)	294(3)	46(1)	1.06
F(2)	2675(3)	6173(2)	1798(3)	48(1)	1.03
F(3)	5733(3)	3382(2)	2418(3)	54(1)	1.06
F(4)	10803(3)	5118(2)	8906(3)	60(1)	1.03
F(5)	6999(3)	2776(2)	4707(4)	56(1)	1.06
F(6)	11325(3)	6085(2)	7211(4)	69(1)	1.04
F(7)	10015(3)	7208(2)	3966(4)	65(1)	1.09
F(8)	9059(4)	8453(2)	4727(3)	75(1)	1.07

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS for $NH_4La(PO_2F_2)_4$. U_{eq} is defined as one-third of the trace of the orthogonalizedU_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
La(1)	2206(1)	822(1)	10165(1)	19(1)	3.23
P(1)	3840(1)	2656(1)	8523(1)	29(1)	5.32
P(2)	-1151(1)	535(1)	7010(1)	26(1)	4.99
P(3)	899(1)	-1544(1)	9165(1)	26(1)	5.06
P(4)	4195(1)	-172(1)	7716(1)	29(1)	5.13
O(1)	202(3)	894(2)	7776(3)	32(1)	1.86
O(2)	-1608(3)	-297(2)	7457(3)	30(1)	1.82
O(3)	1389(3)	-683(2)	9715(4)	33(1)	1.94
O(4)	-417(3)	-1844(2)	9341(4)	32(1)	1.84
O(5)	5620(3)	-130(2)	8651(3)	36(1)	2.02
O(6)	3141(3)	395(2)	8008(3)	33(1)	1.86
O(7)	2786(4)	2154(2)	8953(4)	44(1)	1.90
O(8)	3453(3)	3147(2)	7139(4)	50(1)	2.03
F(1)	-2246(3)	1218(2)	6914(4)	48(1)	1.04
F(2)	848(3)	-1624(2)	7494(3)	54(1)	1.01
F(3)	1992(3)	-2215(2)	9833(4)	56(1)	1.05
F(4)	-1241(3)	467(2)	5306(3)	47(1)	0.96
F(5)	3696(3)	-1095(2)	7656(6)	83(1)	1.06
F(6)	4161(3)	-49(3)	6074(3)	75(1)	1.06
F(7)	4499(5)	3267(3)	9806(5)	101(1)	1.07
F(8)	5022(3)	2088(3)	8554(6)	91(1)	1.15
N(1)	8476(5)	6472(3)	9540(5)	36(1)	

Table S3. Selected bond distances (Å) and angles (deg) for $KLa(PO_2F_2)_4$

K(1)-O(2)	2.724(3)	P(3)-F(4)	1.529(3)
K(1)-O(1)#1	2.834(3)	P(4)-O(8)	1.460(3)
K(1)-O(6)#2	2.877(3)	P(4)-O(5)	1.467(3)
K(1)-F(8)#3	2.970(4)	P(4)-F(7)	1.507(3)
K(1)-O(5)#3	2.988(3)	P(4)-F(8)	1.540(3)
K(1)-F(1)#4	2.990(3)	O(3)-P(1)-O(1)	122.11(17)
K(1)-F(3)#4	3.026(3)	O(3)-P(1)-F(2)	109.74(16)
K(1)-O(5)#1	3.064(3)	O(1)-P(1)-F(2)	109.66(17)
K(1)-O(8)#1	3.224(3)	O(3)-P(1)-F(1)	107.61(16)
K(1)-F(1)#1	3.247(3)	O(1)-P(1)-F(1)	106.17(16)
La(1)-O(4)	2.430(3)	F(2)-P(1)-F(1)	98.96(16)
La(1)-O(7)	2.469(3)	O(7)-P(2)-O(2)	118.99(17)
La(1)-O(8)#5	2.498(3)	O(7)-P(2)-F(5)	110.40(17)
La(1)-O(5)	2.511(3)	O(2)-P(2)-F(5)	108.82(16)
La(1)-O(6)#6	2.531(3)	O(7)-P(2)-F(3)	109.00(17)
La(1)-O(3)#3	2.546(3)	O(2)-P(2)-F(3)	108.61(16)
La(1)-O(1)	2.550(3)	F(5)-P(2)-F(3)	99.19(18)
La(1)-O(2)#3	2.557(3)	O(4)-P(3)-O(6)	121.20(17)
P(1)-O(3)	1.466(3)	O(4)-P(3)-F(6)	109.39(17)
P(1)-O(1)	1.473(3)	O(6)-P(3)-F(6)	108.41(17)
P(1)-F(2)	1.526(3)	O(4)-P(3)-F(4)	108.43(17)
P(1)-F(1)	1.552(3)	O(6)-P(3)-F(4)	107.71(16)
P(2)-O(7)	1.463(3)	F(6)-P(3)-F(4)	99.5(2)
P(2)-O(2)	1.470(3)	O(8)-P(4)-O(5)	118.59(18)
P(2)-F(5)	1.518(3)	O(8)-P(4)-F(7)	109.87(17)
P(2)-F(3)	1.539(3)	O(5)-P(4)-F(7)	109.73(17)
P(3)-O(4)	1.463(3)	O(8)-P(4)-F(8)	109.19(18)
P(3)-O(6)	1.475(3)	O(5)-P(4)-F(8)	107.26(19)
P(3)-F(6)	1.523(3)	F(7)-P(4)-F(8)	100.7(2)

Symmetry transformations used to generate equivalent atoms:

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

Table S4. Selected bond distances (Å) and angles (deg) for $NH_4La(PO_2F_2)_4$

La(1)-O(1)#1	2.571(3)	N(1)-H(1A)	0.847(11)
La(1)-O(2)	2.545(3)	N(1)-H(1B)	0.834(11)
La(1)-O(3)#2	2.527(3)	N(1)-H(1C)	0.848(11)
La(1)-O(4)#1	2.554(3)	N(1)-H(1D)	0.840(11)
La(1)-O(5)#3	2.499(3)	O(4)-P(1)-F(1)	108.26(19)
La(1)-O(6)	2.478(3)	O(4)-P(1)-F(4)	109.10(19)
La(1)-O(7)	2.473(3)	O(7)-P(1)-O(4)	118.75(19)
La(1)-O(8)	2.433(3)	O(7)-P(1)-F(1)	109.36(19)
P(1)-O(4)	1.469(3)	O(7)-P(1)-F(4)	110.0(2)
P(1)-O(7)	1.466(3)	F(4)-P(1)-F(1)	99.6(2)
P(1)-F(1)	1.534(3)	O(1)-P(2)-F(2)	109.74(18)
P(1)-F(4)	1.524(3)	O(1)-P(2)-F(3)	107.03(18)
P(2)-O(1)	1.472(3)	O(2)-P(2)-O(1)	121.89(19)
P(2)-O(2)	1.466(3)	O(2)-P(2)-F(2)	109.84(19)
P(2)-F(2)	1.529(3)	O(2)-P(2)-F(3)	106.76(18)
P(2)-F(3)	1.552(3)	F(2)-P(2)-F(3)	99.04(19)
P(3)-O(3)	1.475(3)	O(3)-P(3)-F(5)	107.4(2)
P(3)-O(8)	1.451(3)	O(3)-P(3)-F(6)	107.8(2)
P(3)-F(5)	1.519(3)	O(8)-P(3)-O(3)	121.43(19)
P(3)-F(6)	1.517(4)	O(8)-P(3)-F(5)	108.5(2)
P(4)-O(5)	1.471(3)	O(8)-P(3)-F(6)	109.7(2)
P(4)-O(6)	1.444(3)	F(6)-P(3)-F(5)	99.9(3)
P(4)-F(7)	1.488(4)	O(5)-P(4)-F(7)	109.4(2)
P(4)-F(8)	1.517(4)	O(5)-P(4)-F(8)	109.1(2)
O(1)-La(1)#1	2.571(3)	O(6)-P(4)-O(5)	118.3(2)
O(3)-La(1)#2	2.527(3)	O(6)-P(4)-F(7)	110.4(2)
O(4)-La(1)#1	2.554(3)	O(6)-P(4)-F(8)	108.7(3)
O(5)-La(1)#4	2.499(3)	F(7)-P(4)-F(8)	99.3(3)

Symmetry transformations used to generate equivalent atoms:

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

Table S5. Hydrogen coordinates and isotropic displacement parameters of $NH_4La(PO_2F_2)_4$.

Atom	x	y	z	U(eq)
H(1A)	3080(40)	8899(19)	-6110(30)	45
H(1B)	3920(30)	8770(20)	-4670(30)	45
H(1C)	2840(30)	8220(20)	-5290(40)	45
H(1D)	3980(30)	8210(20)	-5800(40)	45

Table S6. Hydrogen bonds for $NH_4La(PO_2F_2)_4$. D, donor; H, hydrogen; A, acceptor.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(3)#5	0.847(11)	2.132(14)	2.966(5)	168(4)
N(1)-H(1B)...O(1)	0.834(11)	2.61(3)	3.271(5)	137(3)
N(1)-H(1B)...F(1)	0.834(11)	2.44(3)	3.093(5)	136(3)
N(1)-H(1C)...O(5)#1	0.848(11)	2.26(2)	3.017(5)	149(3)
N(1)-H(1D)...O(4)#7	0.840(11)	2.20(3)	2.874(5)	137(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z	#5 x-1,y,z-1	#7 x,-y+3/2,z-1/2

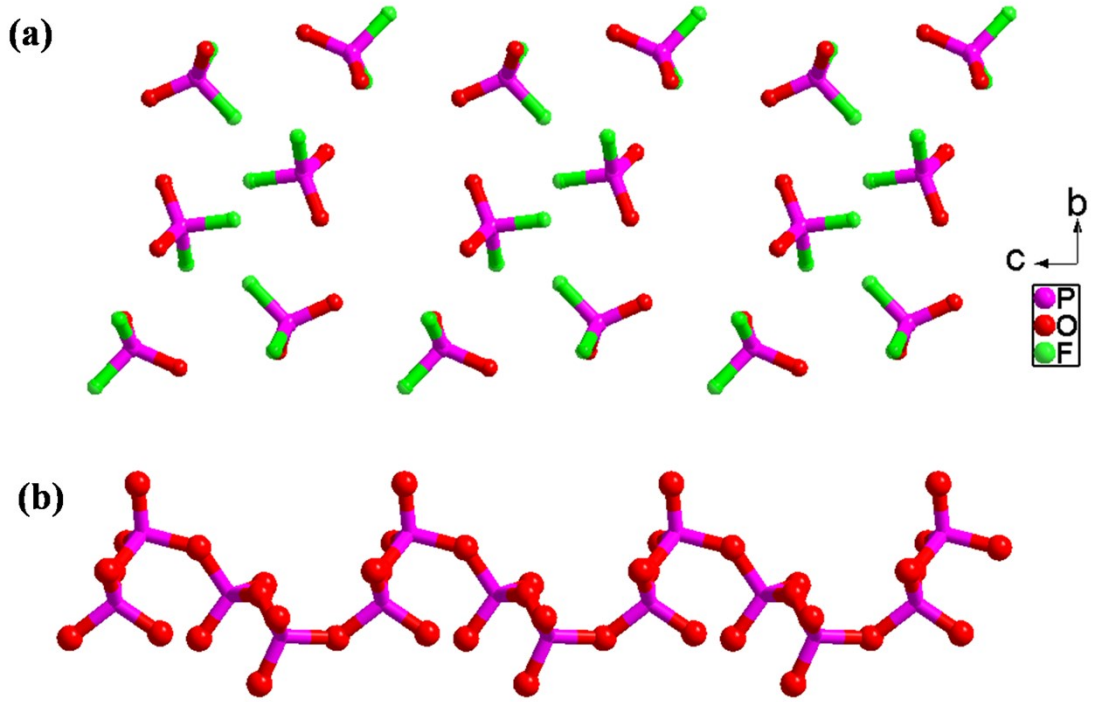

Figure S1. (a) The isolated $[PO_2F_2]^-$anionic structures in $KLa(PO_2F_2)_4$;(b) the infinite $[PO_3]_\infty$ chain structures in $KLa(PO_3)_4$.

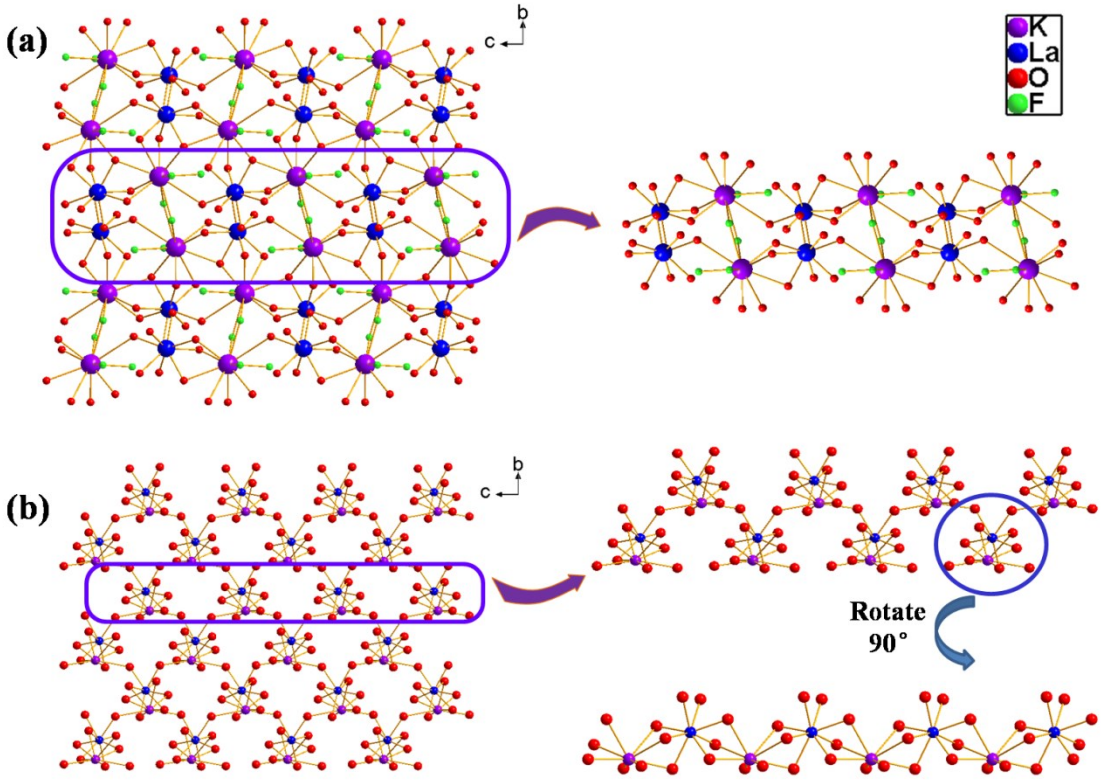

Figure S2. (a)The layered K-La-P-O-F based cationic framework viewed along the *a*-axis. **(b)** The layered K-La-P-O based cationic framework viewed along the *a*-axis

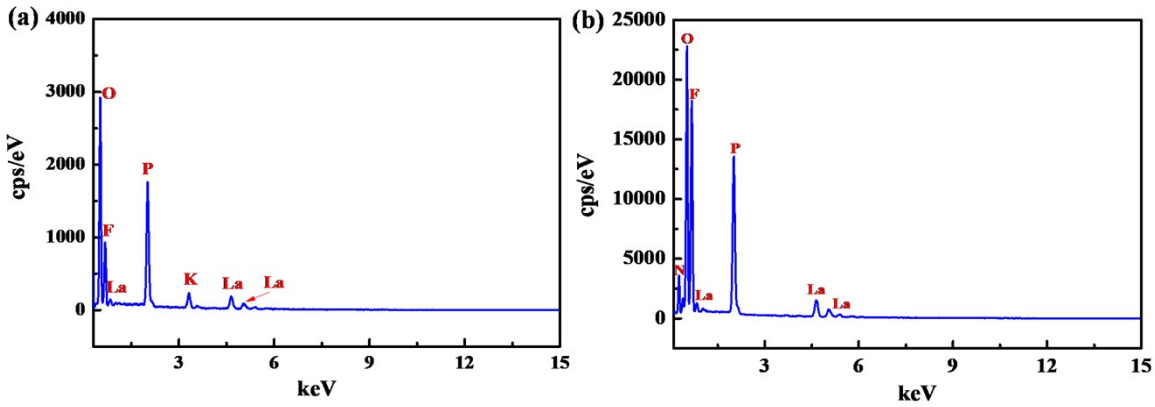

Figure S3. Energy dispersive X-ray spectroscopy of the as-synthesized (a) $KLa(PO_2F_2)_4$ and (b) $NH_4La(PO_2F_2)_4$.

Birefringence Measurements.

The birefringences of $ALa(PO_2F_2)_4$ were characterized by using the polarizing microscope equipped (ZEISS Axio Scope A1) with Berek compensator. The wavelength of the light source was 546 nm. Before the scanning, the small and transparent $ALa(PO_2F_2)_4$ lamellar crystals were chosen to measure, in order to improve the accuracy of the birefringences. The formula for calculating the birefringence is listed below,

$$R = | N_e - N_o | \times T = \Delta n \times T \quad \text{Eq. (1)}$$

Here, R represents the optical path difference, Δn means the birefringence, and T denotes the thickness of the crystal.

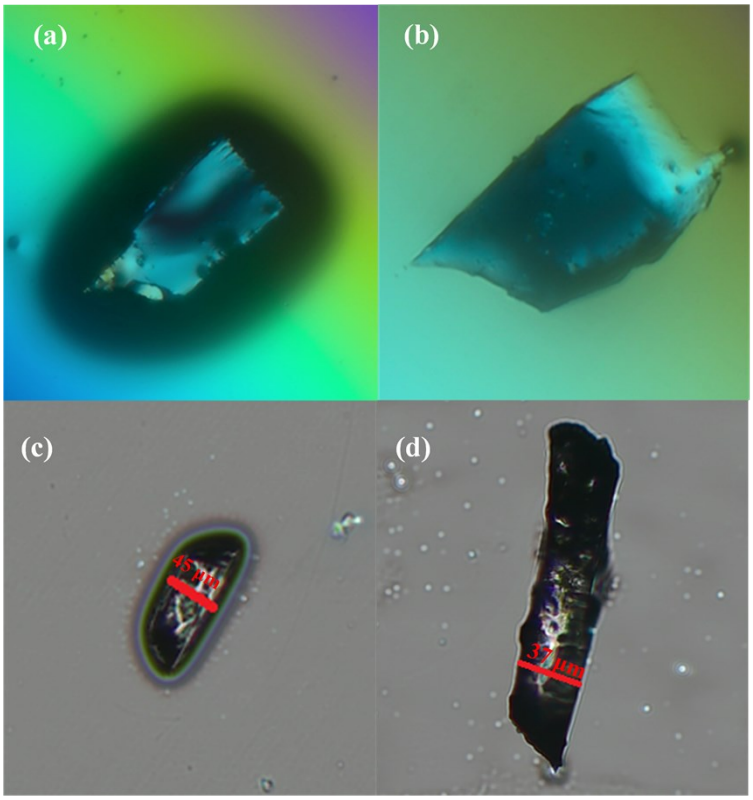

Figure S4. Birefringence measurements on the title crystals. (a, b) $KLa(PO_2F_2)_4$ and $NH_4La(PO_2F_2)_4$ single crystals under the polarizing microscope. (c, d) The thickness of $KLa(PO_2F_2)_4$ and $NH_4La(PO_2F_2)_4$ crystals, respectively.

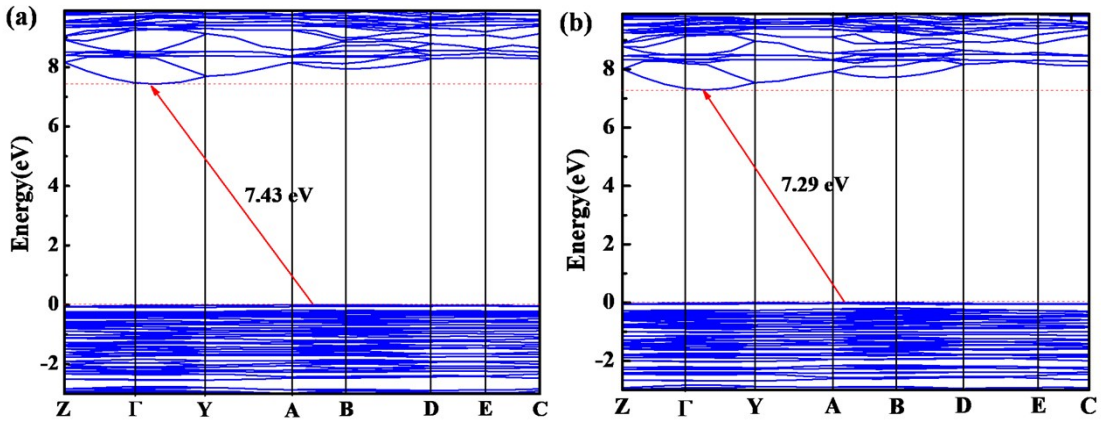

Figure S5. The band structures (HSE06) of (a) $KLa(PO_2F_2)_4$ and (b) $NH_4La(PO_2F_2)_4$