Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

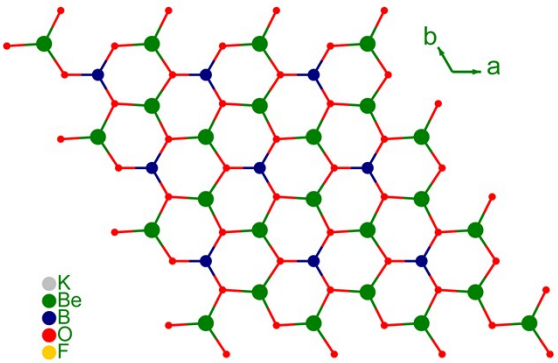

Fig. S1 Honeycomb-like $[Be_2BO_3F_2]_\infty$ layer in the crystal structure of $KBe_2BO_3F_2$.

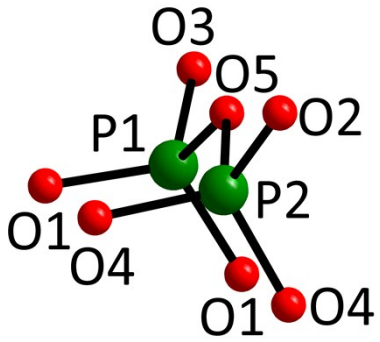

Fig. S2 $[P_2O_7]^{4-}$ dimers with an eclipsed configuration.

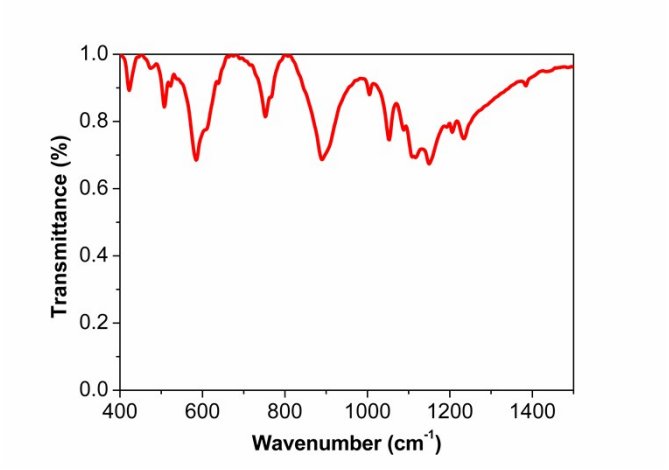

Fig. S3 IR spectra of crystalline $CsNaMgP_2O_7$.

Table S1. Crystal data and structure refinement for $CsNaMgP_2O_7$

Formula sum	$CsNaMgP_2O_7$
Formula weight (g/mol)	354.15
Crystal color	colorless
Crystal size/mm	0.13 × 0.10 × 0.05
Crystal system	orthorhombic
Space group	$Cmc2_1$ (36)
a/Å	5.2361(3)
b/Å	14.9642(9)
c/Å	9.7002(5)
V/Å^3	760.05(7)
Z	4
μ/mm^{-1}	5.425
F(000)	656
Data/restraints/parameters	730/1/67
R(int)	0.0491
GOF(F^2)	1.041
Flack parameter	-0.04(4)
Final R indices [$F_o^2 > 2\sigma(F_c^2)$][a]	R_1 = 0.0329, wR_2 = 0.0807
Final R indices (all data)[a]	R_1 = 0.0348, wR_2 = 0.0828

[a] $R_1 = \sum_2 \left||F_O| - |F_C|\right| / \sum |F_O|$ and $wR_2 = \left[\sum w\left(F_O^2 - F_C^2\right) / \sum wF_O^4\right]^{1/2}$ for $F_o^2 > 2\sigma(F_c^2)$.

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for $CsNaMgP_2O_7$

Atom	Wyck.	Site	*x/a*	*y/b*	*z/c*	*U* [Å^2]
Cs1	4a	m..	0	0.40553(4)	0.84821(5)	0.0227(2)
Na1	4a	m..	1/2	0.3587(3)	0.5163(4)	0.0248(11)
Mg1	4a	m..	1/2	0.1863(3)	0.7540(3)	0.0116(7)
P1	4a	m..	0	0.22098(19)	0.5654(3)	0.0122(6)
P2	4a	m..	0	0.06013(19)	0.7207(3)	0.0110(6)
O1	8b	1	0.2394(15)	0.2525(5)	0.6329(8)	0.044(2)
O2	4a	m..	0	-0.0359(5)	0.6843(9)	0.0232(19)
O3	4a	m..	0	0.2404(7)	0.4162(10)	0.055(4)
O4	8b	1	0.2360(11)	0.0920(4)	0.7968(7)	0.0225(14)
O5	4a	m..	0	0.1129(5)	0.5735(8)	0.0169(17)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Selected bond distances (Å) and angles (deg.) for $CsNaMgP_2O_7$

bonds	Distances (Å)	bonds	Distances (Å)	O-P-O	Angles (deg.)
Cs1—O4^{i}	3.154(6)	P1—O3	1.476(10)	O1—P1—O5	107.1(4)
Cs1—O4^{ii}	3.154(6)	P1—O1	1.491(7)	O1^{iv}—P1—O5	107.1(4)
Cs1—O2^{ii}	3.186(5)	P1—O1^{iv}	1.491(7)	O3—P1—O1	111.6(4)
Cs1—O2^{iii}	3.186(5)	P1—O5	1.619(8)	O3—P1—O1^{iv}	111.6(4)
Cs1—O1^{iv}	3.343(9)	P2—O2	1.479(8)	O1—P1—O1^{iv}	114.5(7)
Cs1—O1	3.343(9)	P2—O4	1.516(6)	O3—P1—O5	104.2(5)
Cs1—O5^{v}	3.422(5)	P2—O4^{iv}	1.516(6)	O2—P2—O4	114.9(3)
Cs1—O5^{vi}	3.422(5)	P2—O5	1.631(8)	O2—P2—O4^{iv}	114.9(3)
Cs1—O3^{vi}	3.473(7)	Na1—O2^{iii}	2.269(9)	O4—P2—O4^{iv}	109.1(5)
Cs1—O3^{v}	3.473(7)	Na1—O1	2.380(9)	O2—P2—O5	105.2(5)
Mg1— O4	2.019(6)	Na1—O1^{xii}	2.380(9)	O4—P2—O5	105.9(3)
Mg1— O1	2.055(7)	Na1—O4^{xi}	2.570(7)	O4^{iv}—P2—O5	105.9(3)
Mg1—O3^{v}	1.918(10)	Na1—O4^{xiii}	2.570(7)		
Mg1—O4^{xii}	2.019(6)				
Mg1—O1^{xii}	2.055(7)				

Symmetry codes: (i) 0.5-x, 0.5+y, z; (ii) -0.5+x, 0.5+y, z; (iii) 0.5+x, 0.5+y, z; (iv) -x, y, z; (v) 0.5-x, 0.5-y, 0.5+z; (vi) -0.5-x, 0.5-y, 0.5+z; (vii) -0.5+x, -0.5+y, z; (viii) 0.5+x, -0.5+y, z; (ix) -1+x, y, z; (x) -0.5-x, 0.5-y, -0.5+z; (xi) 0.5-x, 0.5-y, -0.5+z; (xii) 1-x, y, z; (xiii) 0.5+x, 0.5-y, -0.5+z; (xiv) 1+x, y, z; (xv) 1.5-x, 0.5-y, -0.5+z; (xvi) 1.5-x, 0.5-y, 0.5+z.

Table S4. Anisotropic displacement parameters (Å^2) for $CsNaMgP_2O_7$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs1	0.0164(3)	0.0218(4)	0.0299(4)	0.00000	0.00000	0.0062(4)
Na1	0.038(3)	0.020(2)	0.016(3)	0.00000	0.00000	0.001(2)
Mg1	0.0058(13)	0.0169(19)	0.0119(17)	0.00000	0.00000	-0.0025(15)
P1	0.0073(10)	0.0156(15)	0.0135(13)	0.00000	0.00000	0.0037(11)
P2	0.0072(11)	0.0112(13)	0.0146(14)	0.00000	0.00000	-0.0008(12)
O1	0.035(3)	0.026(3)	0.071(6)	-0.014(3)	-0.038(5)	0.021(5)
O2	0.025(4)	0.013(4)	0.031(5)	0.00000	0.00000	0.000(3)
O3	0.120(11)	0.027(6)	0.018(4)	0.00000	0.00000	0.014(5)
O4	0.013(2)	0.025(3)	0.029(3)	-0.008(2)	-0.005(2)	0.001(2)
O5	0.025(4)	0.013(4)	0.012(4)	0.00000	0.00000	-0.001(3)

Table S5. Comparisons of the Interlayer Bonding for KBBF and $CsNaMgP_2O_7$.

species	bonds	lengths (Å)	q_1[a]	q_2[a]	$\|F\|$[b]
KBBF	K–F	2.755	+1	-1	0.13
$CsNaMgP_2O_7$	Na1—O2^{iii}	2.269	+1	-2	2.95
	Na1—O1	2.380	+1	-2	2.68
	Na1—O1^{xii}	2.380	+1	-2	2.68
	Na1—O4^{xi}	2.570	+1	-2	2.30
	Na1—O4^{xiii}	2.570	+1	-2	2.30
	Cs1–O4^{i}	3.154	+1	-2	1.53
	Cs1–O4^{ii}	3.154	+1	-2	1.53
	Cs1–O2^{ii}	3.186	+1	-2	1.50
	Cs1–O2^{iii}	3.186	+1	-2	1.50
	Cs1–O1^{iv}	3.343	+1	-2	1.36
	Cs1–O1	3.343	+1	-2	1.36
	Cs1–O5^{v}	3.422	+1	-2	1.30
	Cs1–O5^{vi}	3.422	+1	-2	1.30
	Cs1–O3^{vi}	3.473	+1	-2	1.26
	Cs1–O3^{v}	3.473)	+1	-2	1.26

[a]In multiples of 1.602×10^{-19} C. Cations and anions are regarded as ideal point charges with respective expected valence states. [b]In multiples of $|F_{KBBF}|$.

Symmetry codes: (i) 0.5-x, 0.5+y, z; (ii) -0.5+x, 0.5+y, z; (iii) 0.5+x, 0.5+y, z; (iv) -x, y, z; (v) 0.5-x, 0.5-y, 0.5+z; (vi) -0.5-x, 0.5-y, 0.5+z; (xii) 1-x, y, z; (xiii) 0.5+x, 0.5-y, -0.5+z.