Electronic Supplementary Information

Three diphosphates, α-$Li_2Na_2P_2O_7$, $Li_8Pb_3Ba(P_2O_7)_4$ and $Li_7Rb(P_2O_7)_2$: Influences of the cosubstitution on the crystal structure

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Table S1. Crystal data and structure refinements for α-$Li_2Na_2P_2O_7$, $Li_8Pb_3Ba(P_2O_7)_4$, and $Li_7Rb(P_2O_7)_2$.

Empirical formula	α-$Li_2Na_2P_2O_7$	$Li_8Pb_3BaP_8O_{28}$	$Li_7RbP_4O_{14}$
Temperature		296(2) K	
Wavelength		0.71073 Å	
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Ama*2	*C*2/*c*	$P\bar{1}$
Formula weight	233.80	1510.19	459.33
a (Å)	13.272(9)	25.650(4)	5.002(4), α=105.117º
b (Å)	9.007(8)	9.976(13), β=111.33º	6.844(8), β= 102.037º
c (Å)	5.040(3)	9.925 (13)	9.981(9), γ= 102.040º
Z, Volume (Å^3)	4, 602.5(8)	4, 2390.8(6)	4, 309.9(5)
ρ_{Calcd} (Mg/m^3)	2.577	4.196	4.586
μ(/mm)	0.852	23.349	25.0
F(000)	456	2680	230
R(int)	0.0508	0.0336	0.0245
Goodness-of-fit on F^2	1.076	1.066	1.038
Final R indices [$F_o^2>2\sigma(F_o^2)$][a]	R_1 = 0.0386, wR_2= 0.0848	R_1 = 0.0386 wR_2= 0.0839	R_1 = 0.0417 wR_2= 0.0908
R indices (all data)[a]	R_1 = 0.0436, wR_2 = 0.0877	R_1 = 0.0466, wR_2 = 0.0876	R_1 = 0.0519, wR_2 = 0.0966
Largest diff. peak and hole (e·Å^{-3})	0.4 and -0.4	3.3 and -4.8	0.5 and -0.7

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2a. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2× 10^3) for α-$Li_2Na_2P_2O_7$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Li(1)	5800(7)	7153(8)	4630(20)	16(2)
Na(1)	7500	5429(3)	-110(8)	17(1)
Na(2)	5000	5000	10105(7)	20(1)
P(1)	6384(1)	3793(1)	4729(3)	8(1)
O(1)	6300(3)	3873(4)	7710(8)	12(1)
O(2)	6311(3)	5297(4)	3411(8)	13(1)
O(3)	5682(3)	2658(4)	3483(8)	13(1)
O(4)	7500	3134(5)	4027(10)	10(1)

Table S2b. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2× 10^3) for $Li_8Pb_3Ba(P_2O_7)_4$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Pb(1)	5000	5583(1)	7500	7(1)
Pb(2)	2669(1)	12149(1)	3192(1)	22(1)
Ba(1)	5000	9832(1)	7500	12(1)
P(1)	4424(1)	6985(2)	3966(2)	5(1)
P(2)	2078(1)	9529(2)	4737(2)	4(1)
P(3)	5595(1)	7527(2)	5439(2)	3(1)
P(4)	3253(1)	9873(2)	6131(3)	5(1)
Li(1)	6099(7)	10304(17)	5827(19)	11(3)
Li(2)	3613(7)	4744(18)	3298(19)	13(3)
Li(3)	3662(7)	2929(19)	6250(18)	11(3)
Li(4)	3856(7)	7344(18)	6316(18)	10(3)
O(1)	5542(3)	8968(7)	4986(8)	12(2)
O(2)	2716(3)	9116(7)	5046(7)	5(1)
O(3)	5086(3)	6729(7)	4289(7)	7(1)
O(4)	2036(3)	10999(7)	4326(8)	10(1)
O(5)	4148(3)	5922(7)	2864(7)	10(1)
O(6)	3242(3)	9644(8)	7639(7)	11(1)
O(7)	4293(3)	8386(7)	3387(8)	14(2)
O(8)	6108(3)	6812(7)	5394(7)	9(1)
O(9)	4335(3)	6740(8)	5383(8)	13(2)
O(10)	3740(3)	9203(7)	5881(7)	8(1)
O(11)	1755(3)	8652(7)	3491(7)	8(1)
O(12)	5512(3)	7378(7)	6887(7)	8(1)
O(13)	1961(3)	9292(8)	6116(7)	13(2)
O(14)	3186(3)	11341(7)	5706(8)	14(2)

Table S2c. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2× 10^3) for $Li_7Rb(P_2O_7)_2$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Rb(1)	10000	5000	5000	28(1)
Li(1)	8837(15)	10053(11)	6122(7)	16(2)
Li(2)	6150(30)	1660(30)	-292(16)	20(3)
Li(3)	-2970(30)	4240(30)	327(15)	21(3)
Li(4)	9140(30)	6170(20)	1092(14)	11(2)
Li(5)	3330(30)	140(20)	-1167(15)	19(3)
Li(6)	9720(30)	8230(20)	1368(16)	21(3)
P(1)	2121(2)	2582(2)	1687(1)	8(1)
P(2)	5049(2)	7048(2)	2872(1)	9(1)
O(1)	4308(6)	4662(4)	2956(3)	13(1)
O(2)	7526(6)	8279(4)	4180(3)	14(1)
O(3)	269(6)	3362(5)	643(3)	15(1)
O(4)	5890(6)	6922(5)	1475(3)	16(1)
O(5)	2373(6)	7726(5)	2857(3)	19(1)
O(6)	453(6)	1417(5)	2469(3)	19(1)
O(7)	3940(7)	1407(5)	965(3)	22(1)

Table S3a. Selected bond distances (Å) and angles (deg) for α-$Li_2Na_2P_2O_7$.

Li(1)-O(2)	1.906(9)	O(1)#4-Na(1)-O(4)	85.06(14)
Li(1)-O(1)#1	1.944(10)	O(1)#8-Na(1)-O(4)	85.06(14)
Li(1)-O(3)#2	1.999(12)	O(4)#1-Na(1)-O(4)	144.9(2)
Li(1)-O(3)#3	2.057(10)	O(1)#3-Na(2)-O(1)	117.8(3)
Na(1)-O(2)#7	2.378(5)	O(1)#3-Na(2)-O(2)#10	146.82(14)
Na(1)-O(2)	2.378(5)	O(1)-Na(2)-O(2)#10	82.71(14)
Na(1)-O(1)#4	2.389(5)	O(1)#3-Na(2)-O(2)#11	82.71(14)
Na(1)-O(1)#8	2.389(5)	O(1)-Na(2)-O(2)#11	146.82(14)
Na(1)-O(4)#1	2.475(6)	O(2)#10-Na(2)-O(2)#11	93.1(2)
Na(1)-O(4)	2.936(6)	O(1)#3-Na(2)-O(3)#12	88.91(15)
Na(2)-O(1)#3	2.338(4)	O(1)-Na(2)-O(3)#12	72.82(13)
Na(2)-O(1)	2.338(4)	O(2)#10-Na(2)-O(3)#12	123.32(13)
Na(2)-O(2)#10	2.424(5)	O(2)#11-Na(2)-O(3)#12	82.48(13)
Na(2)-O(2)#11	2.424(5)	O(1)#3-Na(2)-O(3)#2	72.82(13)
Na(2)-O(3)#12	2.687(4)	O(1)-Na(2)-O(3)#2	88.91(15)
Na(2)-O(3)#2	2.687(4)	O(2)#10-Na(2)-O(3)#2	82.48(13)
P(1)-O(1)	1.508(4)	O(2)#11-Na(2)-O(3)#2	123.32(13)
P(1)-O(2)	1.511(4)	O(3)#12-Na(2)-O(3)#2	144.6(2)
P(1)-O(3)	1.519(4)	O(1)#3-Na(2)-O(3)#11	75.72(13)
P(1)-O(4)	1.635(2)	O(1)-Na(2)-O(3)#11	149.53(12)
O(2)-Li(1)-O(1)#1	114.6(5)	O(2)#10-Na(2)-O(3)#11	74.71(15)
O(2)-Li(1)-O(3)#2	122.7(5)	O(2)#11-Na(2)-O(3)#11	56.26(13)
O(1)#1-Li(1)-O(3)#2	109.2(4)	O(3)#12-Na(2)-O(3)#11	137.08(16)
O(2)-Li(1)-O(3)#3	108.8(4)	O(3)#2-Na(2)-O(3)#11	68.30(10)
O(1)#1-Li(1)-O(3)#3	96.9(4)	O(1)#3-Na(2)-O(3)#10	149.53(12)
O(3)#2-Li(1)-O(3)#3	100.4(5)	O(1)-Na(2)-O(3)#10	75.72(13)
O(2)#7-Na(1)-O(2)	83.2(2)	O(2)#10-Na(2)-O(3)#10	56.26(13)
O(2)#7-Na(1)-O(1)#4	139.2(2)	O(2)#11-Na(2)-O(3)#10	74.71(15)
O(2)-Na(1)-O(1)#4	82.63(15)	O(3)#12-Na(2)-O(3)#10	68.30(10)
O(2)#7-Na(1)-O(1)#8	82.63(15)	O(3)#2-Na(2)-O(3)#10	137.08(16)
O(2)-Na(1)-O(1)#8	139.2(2)	O(3)#11-Na(2)-O(3)#10	106.88(19)
O(1)#4-Na(1)-O(1)#8	83.6(2)	O(1)-P(1)-O(2)	113.0(2)
O(2)#7-Na(1)-O(4)#1	100.39(16)	O(1)-P(1)-O(3)	113.5(2)
O(2)-Na(1)-O(4)#1	100.39(16)	O(2)-P(1)-O(3)	112.5(2)
O(1)#4-Na(1)-O(4)#1	119.77(16)	O(1)-P(1)-O(4)	107.4(2)
O(1)#8-Na(1)-O(4)#1	119.77(16)	O(2)-P(1)-O(4)	106.7(2)
O(2)#7-Na(1)-O(4)	55.58(14)	O(3)-P(1)-O(4)	102.8(2)
O(2)-Na(1)-O(4)	55.58(14)		

#1 x,y+1/2,z-1/2 #2 x,y+1/2,z+1/2
#3 -x+1,-y+1,z #4 x,y,z-1 #5 -x+1,-y+3/2,z+1/2
#6 -x+1,-y+3/2,z-1/2 #7 -x+3/2,y,z
#8 -x+3/2,y,z-1 #9 x+1/2,-y+1,z-1

#10 x,y,z+1 #11 -x+1,-y+1,z+1 #12 -x+1,-y+1/2,z+1/2
#13 x,y-1/2,z+1/2 #14 x,y-1/2,z-1/2

Table S3b. Selected bond distances (Å) and angles (deg) for $Li_8Pb_3Ba(P_2O_7)_4$.

Pb(1)-O(12)	2.416(7)	O(7)#5-Ba(1)-O(12)	94.59(19)
Pb(1)-O(12)#1	2.416(7)	O(7)#4-Ba(1)-O(12)	161.61(19)
Pb(1)-O(9)#1	2.498(7)	O(1)#4-Ba(1)-O(12)#1	108.2(2)
Pb(1)-O(9)	2.498(7)	O(1)#5-Ba(1)-O(12)#1	115.8(2)
Pb(2)-O(6)#2	2.491(7)	O(7)#5-Ba(1)-O(12)#1	161.61(19)
Pb(2)-O(14)	2.530(7)	O(7)#4-Ba(1)-O(12)#1	94.59(19)
Pb(2)-O(4)	2.542(7)	O(12)-Ba(1)-O(12)#1	67.0(3)
Pb(2)-O(13)#2	2.662(7)	O(1)#4-Ba(1)-O(10)#1	59.52(19)
Pb(1)-O(5)	2.774(8)	O(1)#5-Ba(1)-O(10)#1	133.3(2)
Pb(1)-O(5)#1	2.873(7)	O(7)#5-Ba(1)-O(10)#1	68.64(19)
Pb(1)-O(3)	2.873(7)	O(7)#4-Ba(1)-O(10)#1	127.60(19)
Pb(1)-O(3)#1	2.774(8)	O(12)-Ba(1)-O(10)#1	59.08(18)
Ba(1)-O(1)#4	2.672(7)	O(12)#1-Ba(1)-O(10)#1	100.45(18)
Ba(1)-O(1)#5	2.672(7)	O(1)#4-Ba(1)-O(10)	133.3(2)
Ba(1)-O(7)#5	2.881(8)	O(1)#5-Ba(1)-O(10)	59.52(19)
Ba(1)-O(7)#4	2.881(7)	O(7)#5-Ba(1)-O(10)	127.60(19)
Ba(1)-O(12)	2.937(7)	O(7)#4-Ba(1)-O(10)	68.64(19)
Ba(1)-O(12)#1	2.937(7)	O(12)-Ba(1)-O(10)	100.45(18)
Ba(1)-O(10)#1	3.148(7)	O(12)#1-Ba(1)-O(10)	59.08(18)
Ba(1)-O(10)	3.148(7)	O(10)#1-Ba(1)-O(10)	157.0(2)
P(1)-O(7)	1.505(8)	O(7)-P(1)-O(5)	112.6(4)
P(1)-O(5)	1.517(7)	O(7)-P(1)-O(9)	114.8(4)
P(1)-O(9)	1.518(7)	O(5)-P(1)-O(9)	112.0(4)
P(1)-O(3)	1.637(7)	O(7)-P(1)-O(3)	107.6(4)
P(2)-O(11)	1.513(7)	O(5)-P(1)-O(3)	103.5(4)
P(2)-O(13)	1.514(7)	O(9)-P(1)-O(3)	105.2(4)
P(2)-O(4)	1.516(7)	O(11)-P(2)-O(13)	115.3(4)
P(2)-O(2)	1.613(7)	O(11)-P(2)-O(4)	111.7(4)
P(3)-O(1)	1.499(7)	O(13)-P(2)-O(4)	112.1(4)
P(3)-O(8)	1.509(7)	O(11)-P(2)-O(2)	104.4(4)
P(3)-O(12)	1.531(7)	O(13)-P(2)-O(2)	106.6(4)
P(3)-O(3)	1.625(7)	O(4)-P(2)-O(2)	105.9(4)
P(4)-O(10)	1.511(7)	O(1)-P(3)-O(8)	115.9(4)
P(4)-O(14)	1.518(8)	O(1)-P(3)-O(12)	110.4(4)
P(4)-O(6)	1.524(7)	O(8)-P(3)-O(12)	112.4(4)
P(4)-O(2)	1.620(7)	O(1)-P(3)-O(3)	106.8(4)
Li(1)-O(1)	1.925(18)	O(8)-P(3)-O(3)	104.5(4)
Li(1)-O(10)#5	1.938(18)	O(12)-P(3)-O(3)	106.1(4)
Li(1)-O(7)#5	1.964(19)	O(10)-P(4)-O(14)	113.8(4)
Li(1)-O(6)#1	1.968(19)	O(10)-P(4)-O(6)	112.6(4)
Li(2)-O(5)	1.96(2)	O(14)-P(4)-O(6)	112.3(4)
Li(2)-O(8)#9	2.00(2)	O(10)-P(4)-O(2)	104.5(4)

Li(2)-O(13)#7	2.003(19)	O(14)-P(4)-O(2)	105.9(4)
Li(2)-O(11)#10	2.025(18)	O(6)-P(4)-O(2)	106.9(4)
Li(3)-O(8)#9	1.930(18)	O(1)-Li(1)-O(10)#5	98.2(8)
Li(3)-O(14)#11	1.961(19)	O(1)-Li(1)-O(7)#5	103.2(8)
Li(3)-O(4)#7	1.996(19)	O(10)#5-Li(1)-O(7)#5	117.8(9)
Li(3)-O(5)#12	2.022(19)	O(1)-Li(1)-O(6)#1	114.9(9)
Li(3)-O(7)#12	2.555(19)	O(10)#5-Li(1)-O(6)#1	112.4(9)
Li(4)-O(9)	1.871(18)	O(7)#5-Li(1)-O(6)#1	109.7(9)
Li(4)-O(10)	1.905(19)	O(5)-Li(2)-O(8)#9	119.0(9)
Li(4)-O(11)#7	1.918(18)	O(5)-Li(2)-O(13)#7	114.4(9)
Li(4)-O(12)#1	1.964(18)	O(8)#9-Li(2)-O(13)#7	108.8(9)
O(12)-Pb(1)-O(12)#1	84.3(3)	O(5)-Li(2)-O(11)#10	106.5(9)
O(12)-Pb(1)-O(9)#1	66.1(2)	O(8)#9-Li(2)-O(11)#10	96.4(8)
O(12)#1-Pb(1)-O(9)#1	73.7(2)	O(13)#7-Li(2)-O(11)#10	110.0(9)
O(12)-Pb(1)-O(9)	73.7(2)	O(8)#9-Li(3)-O(14)#11	102.4(8)
O(12)#1-Pb(1)-O(9)	66.1(2)	O(8)#9-Li(3)-O(4)#7	100.8(8)
O(9)#1-Pb(1)-O(9)	124.9(4)	O(14)#11-Li(3)-O(4)#7	86.5(7)
O(6)#2-Pb(2)-O(14)	80.6(2)	O(8)#9-Li(3)-O(5)#12	108.1(8)
O(6)#2-Pb(2)-O(4)	106.6(2)	O(14)#11-Li(3)-O(5)#12	146.7(10)
O(14)-Pb(2)-O(4)	67.7(2)	O(4)#7-Li(3)-O(5)#12	100.2(8)
O(6)#2-Pb(2)-O(13)#2	75.0(2)	O(8)#9-Li(3)-O(7)#12	118.8(8)
O(14)-Pb(2)-O(13)#2	125.8(2)	O(14)#11-Li(3)-O(7)#12	88.6(7)
O(4)-Pb(2)-O(13)#2	74.2(2)	O(4)#7-Li(3)-O(7)#12	140.3(8)
O(1)#4-Ba(1)-O(1)#5	126.8(3)	O(5)#12-Li(3)-O(7)#12	65.4(5)
O(1)#4-Ba(1)-O(7)#5	79.7(2)	O(9)-Li(4)-O(10)	106.2(9)
O(1)#5-Ba(1)-O(7)#5	68.1(2)	O(9)-Li(4)-O(11)#7	125.3(10)
O(1)#4-Ba(1)-O(7)#4	68.1(2)	O(10)-Li(4)-O(11)#7	117.2(9)
O(1)#5-Ba(1)-O(7)#4	79.7(2)	O(9)-Li(4)-O(12)#1	88.6(8)
O(7)#5-Ba(1)-O(7)#4	103.8(3)	O(10)-Li(4)-O(12)#1	101.9(8)
O(1)#4-Ba(1)-O(12)	115.8(2)	O(11)#7-Li(4)-O(12)#1	111.8(9)
O(1)#5-Ba(1)-O(12)	108.2(2)		

#1 -x+1/2,-y+1,z-1/2 #2 x-1/2,y,-z+3/2
#3 -x+1,-y+1,-z+1 #4 -x+3/2,-y+1,z+1/2
#5 -x+1,-y+1,-z+2 #6 -x+1,y+1/2,-z+2
#7 x-1/2,-y+3/2,-z+3/2 #8 x+1/2,-y+3/2,-z+3/2
#9 x+1/2,y,-z+3/2 #10 x,-y+3/2,z
#11 x,-y+1/2,z #12 -x+1/2,-y+1,z+1/2
#13 -x+1,y-1/2,-z+1 #14 -x+3/2,-y+1,z-1/2

Table S3c. Selected bond distances (Å) and angles (deg) for $Li_7Rb(P_2O_7)_2$.

Rb(1)-O(2)#1	2.989(4)	O(1)#2-Rb(1)-O(1)#3	180
Rb(1)-O(2)	2.989(4)	O(2)#1-Rb(1)-O(5)#2	56.11(8)
Rb(1)-O(1)	3.062(3)	O(2)-Rb(1)-O(5)#2	123.89(8)
Rb(1)-O(1)#1	3.062(3)	O(1)-Rb(1)-O(5)#2	99.99(9)
Rb(1)-O(6)#2	3.112(4)	O(1)#1-Rb(1)-O(5)#2	80.01(9)
Rb(1)-O(6)#3	3.112(4)	O(6)#2-Rb(1)-O(5)#2	78.05(11)
Rb(1)-O(1)#2	3.264(3)	O(6)#3-Rb(1)-O(5)#2	101.95(11)
Rb(1)-O(1)#3	3.264(3)	O(1)#2-Rb(1)-O(5)#2	43.91(8)
Rb(1)-O(5)#2	3.418(4)	O(1)#3-Rb(1)-O(5)#2	136.09(8)
Rb(1)-O(5)#3	3.418(4)	O(2)#1-Rb(1)-O(5)#3	123.89(8)
Li(1)-O(5)#4	1.884(8)	O(2)-Rb(1)-O(5)#3	56.11(8)
Li(1)-O(2)	1.890(8)	O(1)-Rb(1)-O(5)#3	80.01(9)
Li(1)-O(6)#2	1.948(8)	O(1)#1-Rb(1)-O(5)#3	99.99(9)
Li(1)-O(2)#5	2.061(8)	O(6)#2-Rb(1)-O(5)#3	101.95(11)
Li(2)-O(7)	1.855(16)	O(6)#3-Rb(1)-O(5)#3	78.05(11)
Li(2)-O(4)#7	1.971(14)	O(1)#2-Rb(1)-O(5)#3	136.09(8)
Li(2)-O(7)#8	2.018(16)	O(1)#3-Rb(1)-O(5)#3	43.91(8)
Li(2)-O(3)#3	2.025(17)	O(5)#2-Rb(1)-O(5)#3	180
Li(3)-O(3)	1.839(15)	O(5)#4-Li(1)-O(2)	132.0(4)
Li(3)-O(4)#11	1.917(15)	O(5)#4-Li(1)-O(6)#2	101.6(4)
Li(3)-O(4)#10	2.149(15)	O(2)-Li(1)-O(6)#2	114.3(4)
Li(3)-O(3)#11	2.430(17)	O(5)#4-Li(1)-O(2)#5	100.6(3)
Li(3)-O(7)#10	2.522(18)	O(2)-Li(1)-O(2)#5	93.0(3)
Li(4)-O(4)	1.886(13)	O(6)#2-Li(1)-O(2)#5	114.1(4)
Li(4)-O(3)#7	1.912(13)	O(7)-Li(2)-O(4)#7	101.2(7)
Li(4)-O(5)#3	1.994(14)	O(7)-Li(2)-O(7)#8	96.2(7)
Li(4)-O(3)#3	2.079(14)	O(4)#7-Li(2)-O(7)#8	124.7(8)
Li(5)-O(7)#8	1.902(15)	O(7)-Li(2)-O(3)#3	115.7(8)
Li(5)-O(6)#13	1.954(16)	O(4)#7-Li(2)-O(3)#3	110.8(8)
Li(5)-O(7)	2.008(14)	O(7)#8-Li(2)-O(3)#3	107.7(7)
Li(5)-O(4)#7	2.084(16)	O(3)-Li(3)-O(4)#11	122.3(8)
Li(6)-O(5)#3	1.931(15)	O(3)-Li(3)-O(4)#10	132.7(8)
Li(6)-O(4)	1.974(16)	O(4)#11-Li(3)-O(4)#10	103.9(7)
Li(6)-O(3)#7	2.021(16)	O(3)-Li(3)-O(3)#11	84.0(6)
Li(6)-O(6)#14	2.085(16)	O(4)#11-Li(3)-O(3)#11	90.4(6)
P(1)-O(6)	1.504(3)	O(4)#10-Li(3)-O(3)#11	86.2(6)
P(1)-O(7)	1.506(3)	O(3)-Li(3)-O(7)#10	96.6(7)
P(1)-O(3)	1.524(3)	O(4)#11-Li(3)-O(7)#10	82.3(6)
P(1)-O(1)	1.631(3)	O(4)#10-Li(3)-O(7)#10	99.2(6)
P(2)-O(5)	1.504(3)	O(3)#11-Li(3)-O(7)#10	171.8(7)
P(2)-O(2)	1.505(3)	O(4)-Li(4)-O(3)#7	111.3(6)
P(2)-O(4)	1.525(3)	O(4)-Li(4)-O(5)#3	106.9(6)

P(2)-O(1)	1.626(3)	O(3)#7-Li(4)-O(5)#3	114.7(7)
O(2)#1-Rb(1)-O(2)	180	O(4)-Li(4)-O(3)#3	134.4(7)
O(2)#1-Rb(1)-O(1)	131.62(8)	O(3)#7-Li(4)-O(3)#3	92.7(6)
O(2)-Rb(1)-O(1)	48.38(8)	O(5)#3-Li(4)-O(3)#3	96.2(6)
O(2)#1-Rb(1)-O(1)#1	48.38(8)	O(7)#8-Li(5)-O(6)#13	117.0(8)
O(2)-Rb(1)-O(1)#1	131.62(8)	O(7)#8-Li(5)-O(7)	95.0(6)
O(1)-Rb(1)-O(1)#1	180	O(6)#13-Li(5)-O(7)	121.4(8)
O(2)#1-Rb(1)-O(6)#2	116.24(10)	O(7)#8-Li(5)-O(4)#7	124.8(8)
O(2)-Rb(1)-O(6)#2	63.76(10)	O(6)#13-Li(5)-O(4)#7	104.4(6)
O(1)-Rb(1)-O(6)#2	94.63(9)	O(7)-Li(5)-O(4)#7	92.6(6)
O(1)#1-Rb(1)-O(6)#2	85.37(9)	O(5)#3-Li(6)-O(4)	105.9(7)
O(2)#1-Rb(1)-O(6)#3	63.76(10)	O(5)#3-Li(6)-O(3)#7	112.6(8)
O(2)-Rb(1)-O(6)#3	116.24(10)	O(4)-Li(6)-O(3)#7	103.4(7)
O(1)-Rb(1)-O(6)#3	85.37(9)	O(5)#3-Li(6)-O(6)#14	95.3(6)
O(1)#1-Rb(1)-O(6)#3	94.63(9)	O(4)-Li(6)-O(6)#14	103.7(7)
O(6)#2-Rb(1)-O(6)#3	180	O(3)#7-Li(6)-O(6)#14	133.4(8)
O(2)#1-Rb(1)-O(1)#2	99.43(8)	O(6)-P(1)-O(7)	114.2(2)
O(2)-Rb(1)-O(1)#2	80.57(8)	O(6)-P(1)-O(3)	112.64(18)
O(1)-Rb(1)-O(1)#2	75.55(10)	O(7)-P(1)-O(3)	111.46(18)
O(1)#1-Rb(1)-O(1)#2	104.45(10)	O(6)-P(1)-O(1)	104.47(17)
O(6)#2-Rb(1)-O(1)#2	45.68(8)	O(7)-P(1)-O(1)	106.37(18)
O(6)#3-Rb(1)-O(1)#2	134.32(8)	O(3)-P(1)-O(1)	107.01(17)
O(2)#1-Rb(1)-O(1)#3	80.57(8)	O(5)-P(2)-O(2)	115.03(18)
O(2)-Rb(1)-O(1)#3	99.43(8)	O(5)-P(2)-O(4)	112.18(17)
O(1)-Rb(1)-O(1)#3	104.45(10)	O(2)-P(2)-O(4)	111.50(18)
O(1)#1-Rb(1)-O(1)#3	75.55(10)	O(5)-P(2)-O(1)	106.09(18)
O(6)#2-Rb(1)-O(1)#3	134.32(8)	O(2)-P(2)-O(1)	104.75(16)
O(6)#3-Rb(1)-O(1)#3	45.68(8)	O(4)-P(2)-O(1)	106.48(16)

#1 -x+2,-y+1,-z+1 #2 -x+1,-y+1,-z+1
#3 x+1,y,z #4 -x+1,-y+2,-z+1 #5 -x+2,-y+2,-z+1
#6 x+1,y+1,z+1 #7 -x+1,-y+1,-z #8 -x+1,-y,-z
#9 -x+2,-y+1,-z #10 x-1,y,z #11 -x,-y+1,-z
#12 -x-1,-y+1,-z #13 -x,-y,-z #14 x+1,y+1,z
#15 x,y+1,z #16 x-1,y-1,z

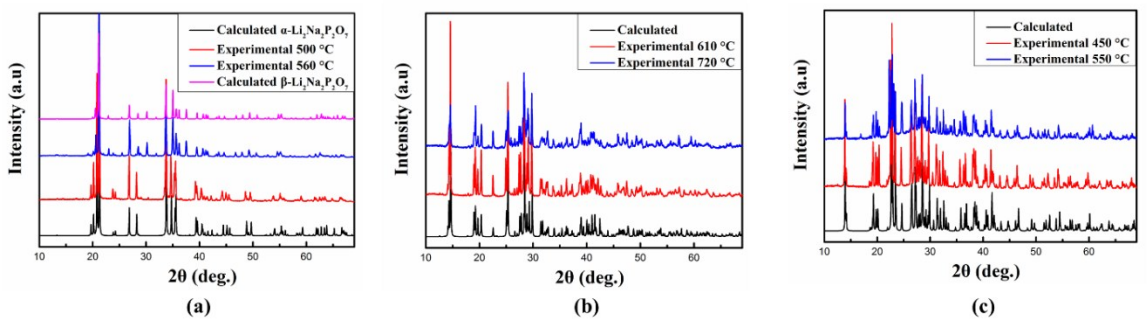

Fig. S1. Experimental and calculated XRD patterns of (a) α-$Li_2Na_2P_2O_7$, (b) $Li_8Pb_3Ba(P_2O_7)_4$, and (c) $Li_7Rb(P_2O_7)_2$.

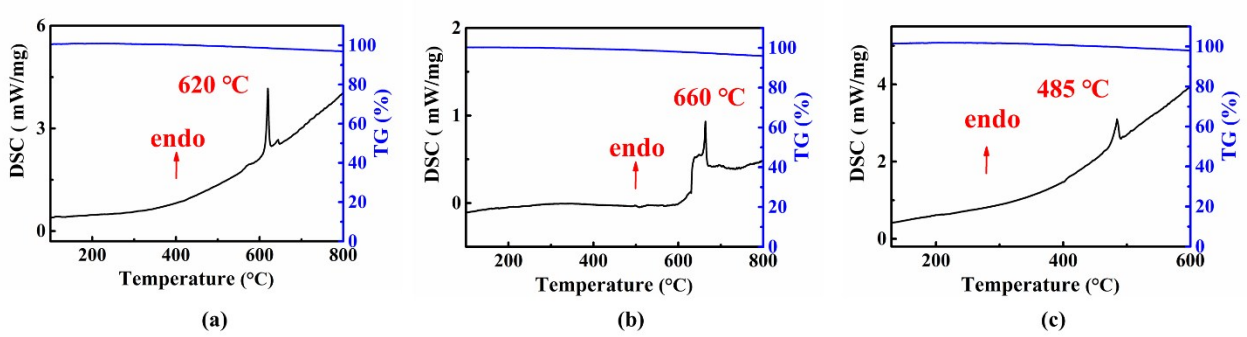

Fig. S2. TG-DSC curves of (a) α-$Li_2Na_2P_2O_7$, (b) $Li_8Pb_3Ba(P_2O_7)_4$, and (c) $Li_7Rb(P_2O_7)_2$.

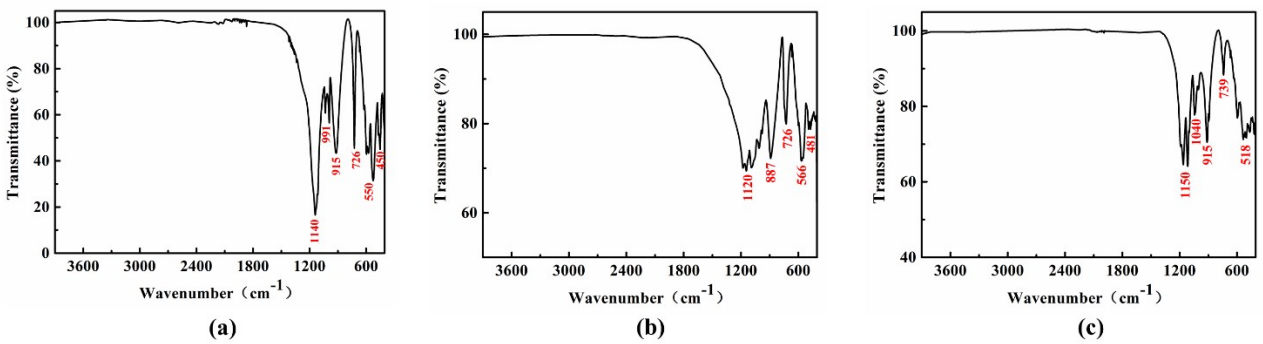

Fig. S3. IR spectra of (a) α-$Li_2Na_2P_2O_7$, (b) $Li_8Pb_3Ba(P_2O_7)_4$, and (c) $Li_7Rb(P_2O_7)_2$.

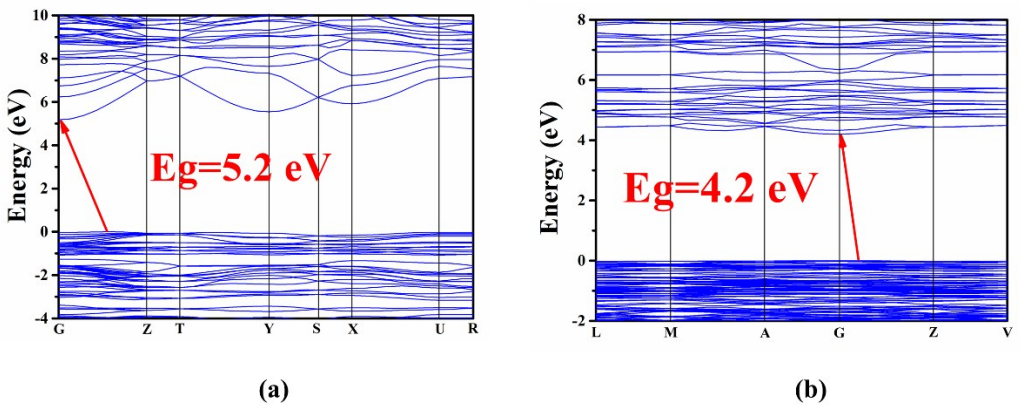

Fig. S4. Band structures of (a) α-$Li_2Na_2P_2O_7$, and (b) $Li_8Pb_3Ba(P_2O_7)_4$.

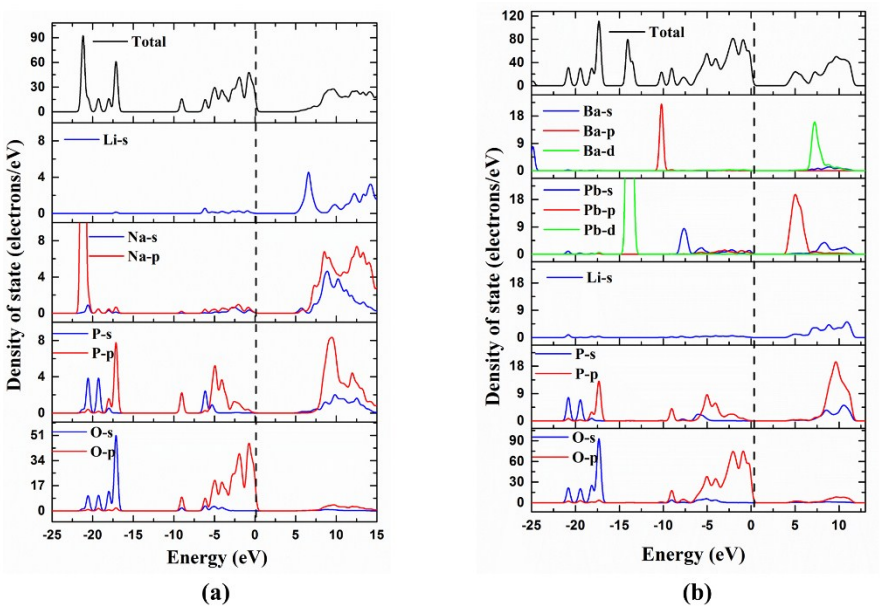

Fig. S5. Projected density of states of (a) α-$Li_2Na_2P_2O_7$, and (b) $Li_8Pb_3Ba(P_2O_7)_4$.