Electronic Supplementary Information

Three New Phosphates, $Cs_8Pb_4(P_2O_7)_4$, $CsLi_7(P_2O_7)_2$ and $LiCa(PO_3)_3$: Structural Comparison, Characterization and Theoretical Calculation

Shujuan Han,[a] Hao Li,[a,b] Zhihua Yang,[a] H. H. Yu*[a] and Shilie Pan*[a]

[a]CAS Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics &Chemistry, CAS; 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.

*Corresponding author, E-mails: slpan@ms.xjb.ac.cn (Shilie Pan).

Table S1. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $Cs_8Pb_4(P_2O_7)_4$, $CsLi_7(P_2O_7)_2$ and $LiCa(PO_3)_3$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	$U_{(eq)}$
		$Cs_8Pb_4(P_2O_7)_4$		
Cs(1)	-4532(1)	8384(1)	6185(1)	29(1)
Cs(2)	2025(1)	7937(1)	2398(1)	27(1)
Cs(3)	-2175(1)	7148(1)	2443(1)	30(1)
Cs(4)	10293(1)	1153(1)	3948(1)	27(1)
Cs(5)	13746(1)	-1866(1)	4265(1)	23(1)
Cs(6)	15874(1)	-3306(1)	663(1)	27(1)
Cs(7)	17390(1)	-178(1)	-91(1)	27(1)
Cs(8)	15573(1)	3255(1)	1422(1)	27(1)
Pb(1)	9966(1)	3795(1)	967(1)	20(1)
Pb(2)	18652(1)	597(1)	1977(1)	16(1)
Pb(3)	11341(1)	4408(1)	3104(1)	17(1)
Pb(4)	2936(1)	4890(1)	5084(1)	20(1)
P(1)	-1926(4)	8879(2)	4113(2)	17(1)
P(2)	-159(3)	6639(2)	4509(2)	16(1)
P(3)	5061(3)	5212(3)	3191(2)	18(1)
P(4)	7724(3)	3456(2)	3149(2)	16(1)
P(5)	10460(4)	7874(2)	383(2)	19(1)
P(6)	12012(4)	5624(2)	872(2)	19(1)
P(7)	12291(3)	1851(3)	1855(2)	18(1)
P(8)	14734(4)	-44(2)	1927(2)	19(1)
O(1)	-2205(9)	9767(7)	4779(5)	32(2)
O(2)	-3120(9)	8176(7)	4223(5)	28(2)
O(3)	-1353(10)	9359(7)	3217(5)	31(2)
O(4)	-426(8)	7994(6)	4232(5)	20(2)
O(5)	-1051(9)	6519(6)	5417(5)	27(2)
O(6)	-655(9)	5973(6)	3908(5)	21(2)
O(7)	1502(9)	6356(6)	4382(5)	26(2)
O(8)	4131(9)	4284(7)	3278(5)	30(2)
O(9)	4844(9)	6198(6)	2575(5)	28(2)
O(10)	6798(8)	4595(6)	2795(4)	16(2)
O(11)	7178(9)	3424(6)	4107(5)	27(2)
O(12)	7465(9)	2425(6)	2755(5)	30(2)
O(13)	9295(9)	3659(7)	2838(5)	28(2)

O(14)	9263(8)	7182(6)	383(5)	20(2)
O(15)	10014(9)	8759(6)	1069(5)	28(2)
O(16)	11120(10)	8349(7)	-496(5)	39(3)
O(17)	11856(8)	6986(6)	590(5)	23(2)
O(18)	13591(9)	5260(7)	850(6)	33(2)
O(19)	10909(10)	5518(7)	1724(5)	35(2)
O(20)	11528(9)	5029(6)	211(5)	22(2)
O(21)	12157(9)	2718(6)	1123(5)	29(2)
O(22)	13911(8)	1085(6)	1471(5)	17(2)
O(23)	11181(8)	1041(7)	2034(5)	24(2)
O(24)	12421(9)	2426(6)	2629(5)	20(2)
O(25)	13759(9)	-218(7)	2795(5)	29(2)
O(26)	14922(10)	-987(6)	1312(5)	34(2)
O(27)	16178(10)	350(7)	1911(6)	38(2)
O(28)	5025(8)	5636(6)	4070(5)	21(2)
		$CsLi_7(P_2O_7)_2$		
Cs(1)	2613(1)	2533(1)	4946(1)	21(1)
Li(1)	3838(7)	6140(7)	3965(5)	15(1)
Li(2)	8908(7)	1158(7)	3790(5)	15(1)
Li(3)	6547(7)	5036(6)	301(5)	15(1)
Li(4)	5790(7)	2466(7)	-1366(5)	18(1)
Li(5)	9851(7)	291(7)	1161(5)	15(1)
Li(6)	418(7)	3430(7)	1075(6)	17(1)
Li(7)	2942(8)	1288(7)	9649(6)	23(1)
P(1)	-928(1)	3556(1)	8331(1)	8(1)
P(2)	2164(1)	4938(1)	7211(1)	8(1)
P(3)	5977(1)	1447(1)	1656(1)	8(1)
P(4)	2896(1)	-21(1)	2893(1)	8(1)
O(1)	4444(3)	848(3)	2901(2)	12(1)
O(2)	1709(3)	-77(3)	4209(2)	14(1)
O(3)	1800(3)	1099(3)	1527(2)	12(1)
O(4)	3943(3)	-1677(3)	2898(2)	15(1)
O(5)	-65(3)	1724(3)	9087(2)	15(1)
O(6)	5943(3)	778(3)	548(2)	13(1)
O(7)	7801(3)	684(3)	2442(2)	12(1)
O(8)	5374(3)	3293(3)	1028(2)	14(1)
O(9)	3399(3)	5036(3)	5912(2)	13(1)
O(10)	3129(3)	3673(3)	8614(2)	12(1)

O(11)	1190(3)	6571(3)	7282(2)	14(1)
O(12)	530(3)	4231(3)	7049(2)	11(1)
O(13)	-2692(3)	3987(3)	7576(2)	14(1)
O(14)	-1091(3)	4435(3)	9312(2)	10(1)
		$LiCa(PO_3)_3$		
Ca(1)	9827(1)	7771(1)	8549(1)	11(1)
Li(1)	5364(8)	1621(8)	1689(8)	23(1)
P(1)	8495(1)	2936(1)	7684(1)	9(1)
P(2)	4020(1)	3833(1)	7849(1)	9(1)
P(3)	2202(1)	1535(1)	5500(1)	9(1)
O(1)	9351(3)	4561(3)	8312(3)	17(1)
O(2)	9799(3)	2368(3)	5737(3)	12(1)
O(3)	8440(3)	1183(3)	9062(3)	14(1)
O(4)	6394(3)	3605(3)	7001(3)	16(1)
O(5)	3353(3)	5937(3)	8074(3)	15(1)
O(6)	3631(3)	2362(3)	9459(3)	13(1)
O(7)	3205(3)	3277(3)	6073(3)	12(1)
O(8)	2472(3)	-233(3)	6811(3)	14(1)
O(9)	2778(3)	1416(3)	3471(3)	14(1)

Table S2a. Selected bond lengths (Å) and angles (deg.) for $Cs_8Pb_4(P_2O_7)_4$.

Cs(1)-O(25)#1	3.121(8)	Cs(8)-O(18)	2.994(8)
Cs(1)-O(12)#2	3.137(9)	Cs(8)-O(12)#12	3.180(9)
Cs(1)-O(24)#1	3.137(8)	Cs(8)-O(8)#12	3.206(8)
Cs(1)-O(2)	3.139(8)	Cs(8)-O(22)	3.220(7)
Cs(1)-O(8)#2	3.168(8)	Cs(8)-O(24)	3.386(8)
Cs(1)-O(1)	3.294(8)	Cs(8)-O(16)#11	3.387(9)
Cs(1)-O(27)#1	3.406(9)	Cs(8)-O(10)#12	3.391(7)
Cs(1)-O(5)	3.592(8)	Cs(8)-O(27)	3.421(9)
Cs(1)-O(11)#2	3.720(9)	Cs(8)-O(17)#11	3.532(8)
Cs(2)-O(9)	3.130(7)	Cs(8)-O(21)	3.591(9)
Cs(2)-O(25)#3	3.153(9)	Pb(1)-O(21)	2.302(8)
Cs(2)-O(15)#4	3.253(8)	Pb(1)-O(20)	2.317(8)
Cs(2)-O(4)	3.267(8)	Pb(1)-O(14)#13	2.437(7)
Cs(2)-O(26)#3	3.267(9)	Pb(2)-O(3)#7	2.402(8)
Cs(2)-O(17)#4	3.293(8)	Pb(2)-O(27)	2.459(9)
Cs(2)-O(3)	3.318(8)	Pb(2)-O(12)#12	2.501(7)
Cs(2)-O(19)#4	3.551(9)	Pb(2)-O(23)#12	2.584(8)
Cs(2)-O(7)	3.574(8)	Pb(2)-O(16)#11	2.610(8)
Cs(2)-O(23)#3	3.621(8)	Pb(2)-O(15)#6	2.640(7)
Cs(3)-O(2)	3.078(8)	Pb(3)-O(13)	2.430(8)
Cs(3)-O(19)#4	3.180(9)	Pb(3)-O(24)	2.458(7)
Cs(3)-O(9)#4	3.187(9)	Pb(3)-O(6)#12	2.543(7)
Cs(3)-O(6)	3.222(8)	Pb(3)-O(5)#1	2.544(8)
Cs(3)-O(3)	3.273(9)	Pb(3)-O(19)	2.612(8)
Cs(3)-O(14)#4	3.280(8)	Pb(3)-O(8)#12	2.727(8)
Cs(3)-O(10)#4	3.281(7)	Pb(4)-O(7)	2.415(7)
Cs(3)-O(15)#4	3.355(8)	Pb(4)-O(11)#1	2.432(8)
Cs(4)-O(23)	3.023(8)	Pb(4)-O(28)	2.475(8)
Cs(4)-O(24)	3.044(8)	Pb(4)-O(28)#1	2.636(8)
Cs(4)-O(1)#6	3.083(9)	Pb(4)-O(6)#2	2.664(8)
Cs(4)-O(1)#1	3.132(9)	P(1)-O(2)	1.489(8)
Cs(4)-O(4)#1	3.255(8)	P(1)-O(1)	1.502(8)
Cs(4)-O(5)#1	3.258(8)	P(1)-O(3)	1.524(8)
Cs(4)-O(3)#6	3.304(9)	P(1)-O(4)	1.654(8)
Cs(4)-O(13)	3.455(8)	P(2)-O(5)	1.511(8)
Cs(4)-O(25)	3.498(8)	P(2)-O(7)	1.517(8)
Cs(4)-O(11)	3.575(8)	P(2)-O(6)	1.517(8)
Cs(5)-O(1)#1	2.949(8)	P(2)-O(4)	1.612(7)
Cs(5)-O(28)#6	2.966(7)	P(3)-O(9)	1.497(8)
Cs(5)-O(25)	2.968(8)	P(3)-O(8)	1.501(8)
Cs(5)-O(2)#7	2.980(8)	P(3)-O(28)	1.548(8)
Cs(5)-O(11)#8	3.131(8)	P(3)-O(10)	1.656(8)
Cs(5)-O(7)#6	3.211(8)	P(4)-O(12)	1.500(8)

Cs(5)-O(9)#6	3.525(8)	P(4)-O(13)	1.504(8)
Cs(6)-O(26)	2.893(7)	P(4)-O(11)	1.513(8)
Cs(6)-O(18)#9	2.926(8)	P(4)-O(10)	1.620(7)
Cs(6)-O(20)#10	2.995(7)	P(5)-O(15)	1.509(8)
Cs(6)-O(9)#6	3.062(8)	P(5)-O(16)	1.514(9)
Cs(6)-O(21)#10	3.123(8)	P(5)-O(14)	1.516(8)
Cs(6)-O(14)#6	3.289(8)	P(5)-O(17)	1.629(8)
Cs(6)-O(18)#10	3.376(8)	P(6)-O(18)	1.480(9)
Cs(7)-O(26)	3.048(9)	P(6)-O(19)	1.516(9)
Cs(7)-O(16)#11	3.115(9)	P(6)-O(20)	1.538(8)
Cs(7)-O(22)#10	3.181(8)	P(6)-O(17)	1.620(8)
Cs(7)-O(15)#11	3.229(8)	P(7)-O(23)	1.507(8)
Cs(7)-O(27)	3.236(9)	P(7)-O(24)	1.522(8)
Cs(7)-O(23)#10	3.262(8)	P(7)-O(21)	1.528(8)
Cs(7)-O(26)#10	3.401(9)	P(7)-O(22)	1.626(8)
Cs(7)-O(14)#6	3.426(7)	P(8)-O(25)	1.495(8)
Cs(7)-O(21)#10	3.437(8)	P(8)-O(26)	1.506(8)
Cs(7)-O(15)#6	3.531(8)	P(8)-O(27)	1.524(9)
Cs(7)-O(16)#6	3.569(9)	P(8)-O(22)	1.646(7)
O(25)#1-Cs(1)-O(12)#2	108.9(2)	O(22)-Cs(8)-O(10)#12	137.28(18)
O(25)#1-Cs(1)-O(24)#1	60.45(19)	O(24)-Cs(8)-O(10)#12	104.08(17)
O(12)#2-Cs(1)-O(24)#1	101.8(2)	O(16)#11-Cs(8)-O(10)#12	96.2(2)
O(12)#2-Cs(1)-O(27)#1	63.3(2)	O(18)-Cs(8)-O(27)	147.0(2)
O(24)#1-Cs(1)-O(27)#1	72.81(19)	O(22)-Cs(8)-O(21)	41.59(17)
O(2)-Cs(1)-O(27)#1	159.0(2)	O(24)-Cs(8)-O(21)	42.50(18)
O(8)#2-Cs(1)-O(27)#1	101.8(2)	O(16)#11-Cs(8)-O(21)	122.5(2)
O(1)-Cs(1)-O(27)#1	117.3(2)	O(10)#12-Cs(8)-O(21)	139.41(18)
O(25)#1-Cs(1)-O(5)	103.4(2)	O(27)-Cs(8)-O(21)	84.65(19)
O(9)-Cs(2)-O(25)#3	83.0(2)	O(17)#11-Cs(8)-O(21)	106.41(18)
O(9)-Cs(2)-O(15)#4	141.1(2)	O(21)-Pb(1)-O(20)	82.1(3)
O(25)#3-Cs(2)-O(15)#4	116.47(19)	O(21)-Pb(1)-O(14)#13	81.7(3)
O(9)-Cs(2)-O(4)	107.8(2)	O(20)-Pb(1)-O(14)#13	82.0(3)
O(3)-Cs(2)-O(7)	85.00(18)	O(3)#7-Pb(2)-O(27)	94.6(3)
O(19)#4-Cs(2)-O(7)	83.21(18)	O(3)#7-Pb(2)-O(12)#12	96.3(3)
O(9)-Cs(2)-O(23)#3	134.9(2)	O(27)-Pb(2)-O(12)#12	87.9(3)
O(25)#3-Cs(2)-O(23)#3	54.56(19)	O(27)-Pb(2)-O(15)#6	94.1(3)
O(15)#4-Cs(2)-O(23)#3	64.52(18)	O(12)#12-Pb(2)-O(15)#6	175.9(3)
O(4)-Cs(2)-O(23)#3	93.28(17)	O(23)#12-Pb(2)-O(15)#6	89.7(2)
O(26)#3-Cs(2)-O(23)#3	67.76(18)	O(16)#11-Pb(2)-O(15)#6	83.7(3)
O(17)#4-Cs(2)-O(23)#3	100.67(17)	O(13)-Pb(3)-O(24)	75.9(2)
O(3)-Cs(2)-O(23)#3	60.04(18)	O(13)-Pb(3)-O(6)#12	84.8(2)
O(19)#4-Cs(2)-O(23)#3	133.62(19)	O(24)-Pb(3)-O(6)#12	155.2(3)
O(7)-Cs(2)-O(23)#3	128.08(17)	O(13)-Pb(3)-O(5)#1	94.6(3)

O(2)-Cs(3)-O(19)#4	123.3(2)	O(24)-Pb(3)-O(5)#1	84.1(2)
O(2)-Cs(3)-O(9)#4	96.4(2)	O(6)#12-Pb(3)-O(5)#1	82.0(2)
O(19)#4-Cs(3)-O(9)#4	119.2(2)	O(13)-Pb(3)-O(19)	75.5(3)
O(2)-Cs(3)-O(6)	59.53(19)	O(24)-Pb(3)-O(19)	103.5(3)
O(14)#4-Cs(3)-O(10)#4	102.30(18)	O(7)-Pb(4)-O(6)#2	96.4(2)
O(2)-Cs(3)-O(15)#4	110.5(2)	O(11)#1-Pb(4)-O(6)#2	99.1(2)
O(19)#4-Cs(3)-O(15)#4	72.7(2)	O(28)-Pb(4)-O(6)#2	176.3(2)
O(9)#4-Cs(3)-O(15)#4	137.4(2)	O(28)#1-Pb(4)-O(6)#2	102.9(2)
O(6)-Cs(3)-O(15)#4	111.4(2)	O(2)-P(1)-O(1)	114.7(5)
O(3)-Cs(3)-O(15)#4	63.37(19)	O(2)-P(1)-O(3)	115.4(5)
O(14)#4-Cs(3)-O(15)#4	44.89(18)	O(1)-P(1)-O(3)	112.8(5)
O(10)#4-Cs(3)-O(15)#4	144.56(18)	O(2)-P(1)-O(4)	107.8(4)
O(23)-Cs(4)-O(24)	49.9(2)	O(1)-P(1)-O(4)	103.8(5)
O(23)-Cs(4)-O(1)#6	112.5(2)	O(3)-P(1)-O(4)	100.4(4)
O(3)#6-Cs(4)-O(25)	90.9(2)	O(5)-P(2)-O(7)	114.6(5)
O(13)-Cs(4)-O(25)	107.91(18)	O(5)-P(2)-O(6)	111.9(5)
O(23)-Cs(4)-O(11)	96.78(19)	O(7)-P(2)-O(6)	111.3(4)
O(24)-Cs(4)-O(11)	95.16(19)	O(5)-P(2)-O(4)	107.6(4)
O(1)#6-Cs(4)-O(11)	80.5(2)	O(7)-P(2)-O(4)	103.1(4)
O(1)#1-Cs(4)-O(11)	131.41(19)	O(6)-P(2)-O(4)	107.7(4)
O(4)#1-Cs(4)-O(11)	85.87(18)	O(9)-P(3)-O(8)	117.5(5)
O(5)#1-Cs(4)-O(11)	71.2(2)	O(9)-P(3)-O(28)	112.2(5)
O(3)#6-Cs(4)-O(11)	91.5(2)	O(8)-P(3)-O(28)	111.1(5)
O(13)-Cs(4)-O(11)	41.89(18)	O(9)-P(3)-O(10)	103.2(4)
O(25)-Cs(4)-O(11)	149.59(18)	O(8)-P(3)-O(10)	106.9(4)
P(7)-Cs(4)-O(11)	97.67(13)	O(28)-P(3)-O(10)	104.7(4)
O(1)#1-Cs(5)-O(28)#6	155.1(2)	O(15)-P(5)-O(16)	114.3(5)
O(1)#1-Cs(5)-O(25)	82.1(2)	O(15)-P(5)-O(14)	113.8(5)
O(28)#6-Cs(5)-O(25)	122.7(2)	O(16)-P(5)-O(14)	111.8(5)
O(1)#1-Cs(5)-O(2)#7	101.6(2)	O(15)-P(5)-O(17)	104.9(5)
O(20)#10-Cs(6)-O(18)#10	46.2(2)	O(16)-P(5)-O(17)	102.7(5)
O(9)#6-Cs(6)-O(18)#10	124.9(2)	O(14)-P(5)-O(17)	108.4(4)
O(21)#10-Cs(6)-O(18)#10	64.0(2)	O(18)-P(6)-O(19)	116.5(5)
O(14)#6-Cs(6)-O(18)#10	100.73(19)	O(18)-P(6)-O(20)	113.5(5)
O(15)#11-Cs(7)-O(27)	113.3(2)	O(19)-P(6)-O(20)	108.0(5)
O(26)-Cs(7)-O(23)#10	130.4(2)	O(18)-P(6)-O(17)	104.8(5)
O(16)#11-Cs(7)-O(23)#10	116.1(2)	O(19)-P(6)-O(17)	107.6(5)
O(22)#10-Cs(7)-O(23)#10	46.14(19)	O(20)-P(6)-O(17)	105.6(4)
O(15)#11-Cs(7)-O(23)#10	69.13(19)	O(23)-P(7)-O(24)	115.3(5)
O(27)-Cs(7)-O(23)#10	172.5(2)	O(23)-P(7)-O(21)	113.4(5)
O(26)-Cs(7)-O(26)#10	93.4(2)	O(24)-P(7)-O(21)	112.5(5)
O(16)#11-Cs(7)-O(26)#10	113.3(2)	O(23)-P(7)-O(22)	107.4(4)
O(22)#10-Cs(7)-O(26)#10	43.56(18)	O(24)-P(7)-O(22)	105.3(4)
O(18)-Cs(8)-O(16)#11	134.6(2)	O(21)-P(7)-O(22)	101.4(4)

O(12)#12-Cs(8)-O(16)#11	68.5(2)	O(25)-P(8)-O(26)	115.6(5)
O(8)#12-Cs(8)-O(16)#11	133.5(2)	O(25)-P(8)-O(27)	114.9(5)
O(22)-Cs(8)-O(16)#11	91.3(2)	O(26)-P(8)-O(27)	113.3(5)
O(24)-Cs(8)-O(16)#11	130.44(18)	O(25)-P(8)-O(22)	107.9(4)
O(18)-Cs(8)-O(10)#12	100.20(19)	O(26)-P(8)-O(22)	102.0(5)
O(12)#12-Cs(8)-O(10)#12	44.75(17)	O(27)-P(8)-O(22)	101.1(4)
O(8)#12-Cs(8)-O(10)#12	45.14(19)		

Symmetry transformations used to generate equivalent atoms:

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

#5 x-2, y+1, z #6 x+1, y-1, z #7 x+2, y-1, z #8 -x+2, -y, -z+1

#9 x, y-1, z #10 -x+3, -y, -z #11 -x+3, -y+1, -z #12 x+1, y, z

#13 -x+2, -y+1, -z #14 -x+4, -y, -z #15 x, y+1, z

Table S2b. Selected bond lengths (Å) and angles (deg.) for $CsLi_7(P_2O_7)_2$.

Cs(1)-O(1)	3.077(2)	Li(5)-O(5)#8	1.981(5)
Cs(1)-O(2)	3.125(2)	Li(5)-O(3)#6	1.995(5)
Cs(1)-O(7)#1	3.130(2)	Li(6)-O(11)#2	1.933(5)
Cs(1)-O(9)	3.139(2)	Li(6)-O(3)	1.983(6)
Cs(1)-O(12)	3.178(2)	Li(6)-O(14)#10	1.992(6)
Cs(1)-O(13)#2	3.191(2)	Li(6)-O(14)#2	2.072(6)
Cs(1)-O(12)#2	3.271(2)	Li(7)-O(6)#1	1.941(6)
Cs(1)-O(1)#1	3.312(2)	Li(7)-O(3)#14	1.957(6)
Cs(1)-O(4)#1	3.353(2)	Li(7)-O(10)	2.061(6)
Cs(1)-O(11)#2	3.610(2)	Li(7)-O(5)	2.299(6)
Li(1)-O(9)	1.855(5)	Li(7)-O(6)#14	2.409(6)
Li(1)-O(4)#3	1.881(6)	P(1)-O(5)	1.512(2)
Li(1)-O(13)#2	1.979(5)	P(1)-O(12)	1.627(2)
Li(1)-O(9)#4	2.032(6)	P(1)-O(13)	1.500(2)
Li(2)-O(11)#4	1.912(6)	P(1)-O(14)	1.524(2)
Li(2)-O(2)#1	1.927(5)	P(2)-O(9)	1.501(2)
Li(2)-O(7)	1.980(5)	P(2)-O(10)	1.527(2)
Li(2)-O(2)#6	2.083(6)	P(2)-O(11)	1.504(2)
Li(3)-O(8)	1.913(5)	P(2)-O(12)	1.6290(19)
Li(3)-O(8)#5	1.943(6)	P(3)-O(6)	1.524(2)
Li(3)-O(14)#8	1.970(5)	P(3)-O(7)	1.514(2)
Li(3)-O(10)#4	2.046(5)	P(3)-O(8)	1.501(2)
Li(4)-O(6)	1.919(6)	P(3)-O(1)	1.629(2)
Li(4)-O(13)#8	1.961(5)	P(4)-O(1)	1.6218(19)
Li(4)-O(4)#9	1.972(6)	P(4)-O(2)	1.502(2)
Li(4)-O(10)#10	1.979(6)	P(4)-O(3)	1.519(2)
Li(5)-O(7)	1.934(5)	P(4)-O(4)	1.504(2)
Li(5)-O(5)#1	1.963(5)		
O(1)-Cs(1)-O(2)	47.05(5)	O(5)#1-Li(5)-O(3)#6	130.3(3)
O(1)-Cs(1)-O(7)#1	95.68(6)	O(5)#8-Li(5)-O(3)#6	90.1(2)
O(2)-Cs(1)-O(7)#1	63.79(6)	O(6)#1-Li(7)-O(3)#14	115.4(3)
O(1)-Cs(1)-O(9)	136.53(5)	O(6)#1-Li(7)-O(6)#14	84.0(2)
O(1)#1-Cs(1)-O(11)#2	135.57(5)	O(3)#14-Li(7)-O(6)#14	90.2(2)
O(4)#1-Cs(1)-O(11)#2	178.25(4)	O(10)-Li(7)-O(6)#14	83.3(2)
O(9)-Li(1)-O(4)#3	130.3(3)	O(5)-Li(7)-O(6)#14	172.6(3)
O(9)-Li(1)-O(13)#2	124.2(3)	O(13)-P(1)-O(5)	113.45(12)
O(4)#3-Li(1)-O(13)#2	95.0(2)	O(13)-P(1)-O(14)	113.91(12)
O(9)-Li(1)-O(9)#4	93.8(2)	O(14)-P(1)-O(12)	106.38(11)
O(11)#4-Li(2)-O(7)	102.0(3)	O(9)-P(2)-O(11)	114.68(12)
O(2)#1-Li(2)-O(7)	115.5(3)	O(9)-P(2)-O(10)	112.90(12)

O(11)#4-Li(2)-O(2)#6	105.7(2)	O(11)-P(2)-O(10)	112.21(12)
O(2)#1-Li(2)-O(2)#6	90.3(2)	O(9)-P(2)-O(12)	104.80(11)
O(7)-Li(2)-O(2)#6	114.8(3)	O(11)-P(2)-O(12)	105.82(12)
O(8)-Li(3)-O(8)#5	97.8(2)	O(10)-P(2)-O(12)	105.42(11)
O(8)#5-Li(3)-O(10)#4	99.7(2)	O(8)-P(3)-O(7)	114.40(12)
O(14)#8-Li(3)-O(10)#4	108.8(2)	O(8)-P(3)-O(1)	106.13(12)
O(7)-Li(5)-O(5)#1	111.2(2)	O(7)-P(3)-O(1)	104.24(11)
O(7)-Li(5)-O(5)#8	123.9(3)	O(6)-P(3)-O(1)	107.24(11)
O(5)#1-Li(5)-O(5)#8	96.1(2)	O(2)-P(4)-O(4)	114.81(12)
O(7)-Li(5)-O(3)#6	105.3(2)	O(3)-P(4)-O(1)	106.21(11)

Symmetry transformations used to generate equivalent atoms:

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

#6 x+1,y,z #7 -x+2,-y,-z+1 #8 x+1,y,z-1 #9 -x+1,-y,-z #10 x,y,z-1

#11 -x+2,-y,-z #12 -x,-y+1,-z #13 x-1,y,z #14 x,y,z+1 #15 x-1,y,z+1

#16 -x+1,-y,-z+2 #17 x,y-1,z

Table S2c. Selected bond lengths (Å) and angles (deg.) for $LiCa(PO_3)_3$.

Ca(1)-O(1)	2.316(2)	Li(1)-O(3)#9	2.583(6)
Ca(1)-O(9)#1	2.432(2)	P(1)-O(1)	1.477(2)
Ca(1)-O(3)#2	2.454(2)	P(1)-O(3)	1.493(2)
Ca(1)-O(3)#3	2.471(2)	P(1)-O(4)	1.557(2)
Ca(1)-O(8)#4	2.496(2)	P(1)-O(2)	1.603(2)
Ca(1)-O(5)#5	2.499(2)	P(2)-O(5)	1.478(2)
Ca(1)-O(6)#6	2.529(2)	P(2)-O(6)	1.488(2)
Ca(1)-O(1)#3	2.750(2)	P(2)-O(7)	1.5933(19)
Ca(1)-O(2)#7	3.123(2)	P(2)-O(4)	1.596(2)
Li(1)-O(9)	2.000(6)	P(3)-O(8)	1.481(2)
Li(1)-O(8)#8	2.028(6)	P(3)-O(9)	1.482(2)
Li(1)-O(5)#1	2.035(6)	P(3)-O(7)	1.5838(19)
Li(1)-O(6)#9	2.132(6)	P(3)-O(2)#10	1.612(2)
O(1)-Ca(1)-O(9)#1	84.35(7)	O(1)#3-Ca(1)-O(2)#7	141.00(6)
O(1)-Ca(1)-O(3)#2	150.64(7)	P(1)#3-Ca(1)-O(2)#7	153.70(4)
O(9)#1-Ca(1)-O(3)#2	75.60(7)	O(9)-Li(1)-O(8)#8	102.3(3)
O(1)-Ca(1)-O(3)#3	124.39(7)	O(9)-Li(1)-O(5)#1	112.5(3)
O(9)#1-Ca(1)-O(3)#3	147.58(7)	O(8)#8-Li(1)-O(5)#1	84.3(2)
O(3)#2-Ca(1)-O(3)#3	72.05(7)	O(8)#8-Li(1)-O(3)#9	80.47(19)
O(1)-Ca(1)-O(8)#4	130.21(7)	O(5)#1-Li(1)-O(3)#9	81.22(19)
O(8)#4-Ca(1)-O(5)#5	66.16(7)	O(6)#9-Li(1)-O(3)#9	83.9(2)
O(1)-Ca(1)-O(6)#6	79.57(7)	O(1)-P(1)-O(3)	113.24(12)
O(9)#1-Ca(1)-O(6)#6	72.23(7)	O(3)-P(1)-O(4)	112.46(11)
O(3)#2-Ca(1)-O(6)#6	74.05(7)	O(1)-P(1)-O(2)	108.58(11)
O(3)#3-Ca(1)-O(6)#6	96.60(7)	O(3)-P(1)-O(2)	110.83(11)
O(8)#4-Ca(1)-O(6)#6	148.97(7)	O(4)-P(1)-O(2)	97.92(10)
O(5)#5-Ca(1)-O(6)#6	141.38(7)	O(5)-P(2)-O(6)	119.59(12)
O(1)-Ca(1)-O(1)#3	69.29(8)	O(5)-P(2)-O(7)	108.60(11)
O(9)#1-Ca(1)-O(1)#3	141.27(7)	O(6)-P(2)-O(4)	110.42(11)
O(3)#2-Ca(1)-O(1)#3	114.96(7)	O(7)-P(2)-O(4)	96.77(11)
O(3)#3-Ca(1)-O(1)#3	56.42(6)	O(8)-P(3)-O(9)	120.84(12)
O(8)#4-Ca(1)-O(1)#3	119.49(6)	O(8)-P(3)-O(7)	111.19(11)
O(5)#5-Ca(1)-O(1)#3	68.71(7)	O(9)-P(3)-O(7)	108.42(11)
O(6)#6-Ca(1)-O(1)#3	75.38(6)	O(8)-P(3)-O(2)#10	108.12(11)

Symmetry transformations used to generate equivalent atoms:

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

#6 -x+1, -y+1, -z+2 #7 -x+2, -y+1, -z+1 #8 -x+1, -y, -z+1 #9 x, y, z-1 #10 x-1, y, z

#11 x, y-1, z #12 x, y, z+1 #13 x-1, y-1, z

Table S3. The reported cesium lead phosphates, lithium cesium phosphates and lithium calcium phosphates.

No.	Compounds	Space group	Anionic framework	Cation/ Phosphorus	Cutoff edge (nm)	Reference
			Cs-Pb-P-O system			
1	$Pb_2Cs_3(P_4O_{12})(PO_3)_3$	$P\bar{1}$	Isolated P_4O_{12} and 1D PO_3 chain	0.71	/	1
2	$CsPb(PO_4)$	*Pnma*	Isolated PO_4	2	below 242 nm	2
3	$CsPb_4(PO_4)_3$	$P6_3/m$	Isolated PO_4	1.67	below 300 nm	3
4	$Cs_8Pb_4(P_2O_7)_4$	$P\bar{1}$	Isolated P_2O_7	1.5	below 230 nm	This work
			Cs-Li-P-O system			
1	$LiCs(PO_3)_2$	*Fdd*2	1D PO_3 chain	1	/	4
2	$LiCs_2PO_4$	$Cmc2_1$	Isolated PO_4	3	174 nm/below 190 nm	5-7
3	$CsLi_7(P_2O_7)_2$	$P\bar{1}$	Isolated P_2O_7	2	below 190 nm	This work
			Ca-Li-P-O system			
1	$LiCa(PO_4)$	*P*31*c*	Isolated PO_4	2	/	8
2	$Ca_{10}Li(PO_4)_7$	*R*3*c*	Isolated PO_4	1.57	optical band gap 3.90 eV	9
3	$Ca_{9.95}Li_{1.05}(PO_4)_7$	*R*3*c*	Isolated PO_4	1.57	/	10
4	$LiCa(PO_3)_3$	$P\bar{1}$	1D PO_3 chain	0.67	below 190 nm	This work

Table S4. Comparison of BVS and GII values in different structures

	BVS		GII	
compounds	Ca^{2+}	Zn^{2+}	Ca^{2+}	Zn^{2+}
$LiCa(PO_3)_3$	2.01	0.99	0.13	0.35
$LiZn(PO_3)_3$	4.31	2.12	0.65	0.14

Fig. S1. The arrangement of CsO_n (n = 7-11) in $Cs_8Pb_4(P_2O_7)_4$.

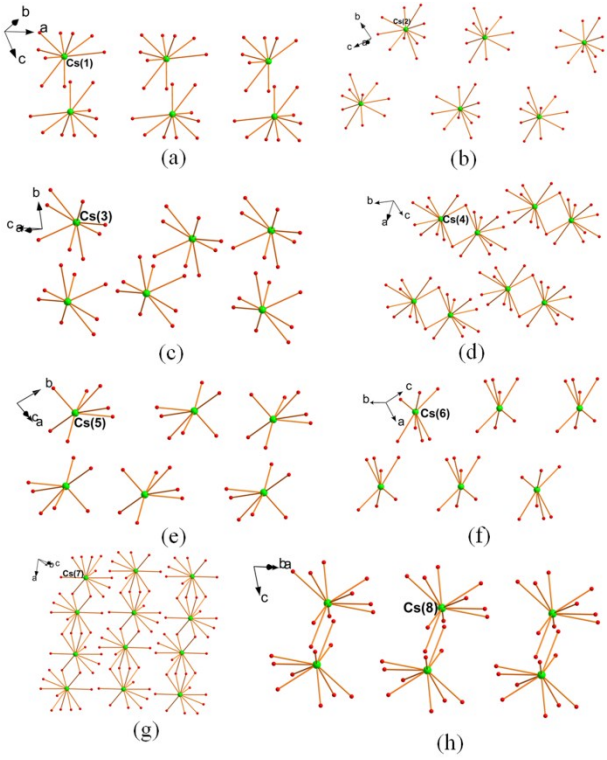


Fig. S2. The arrangement of PbO_n (n = 3, 5, 6) in $Cs_8Pb_4(P_2O_7)_4$.

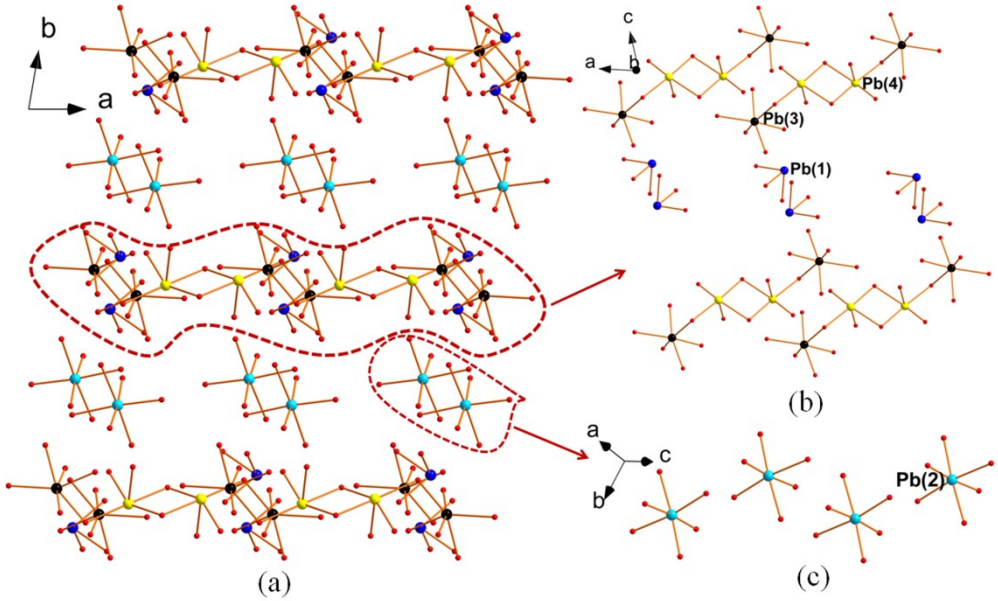


Fig. S3. The arrangement of CsO_{10} and LiO_n (n = 4, 5) in $CsLi_7(P_2O_7)_2$.

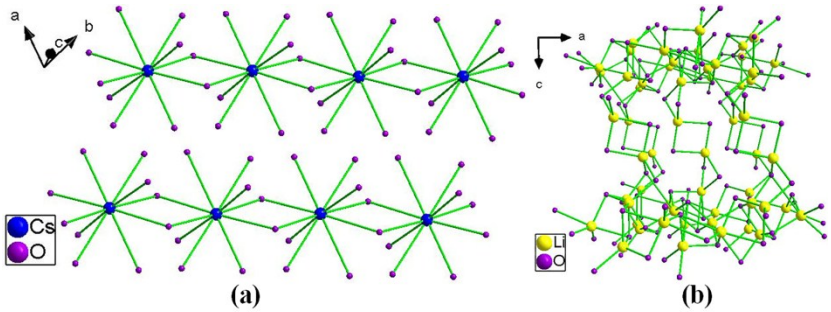


Fig. S4. The arrangement of LiO_5 and CaO_8 in $LiCa(PO_3)_3$.

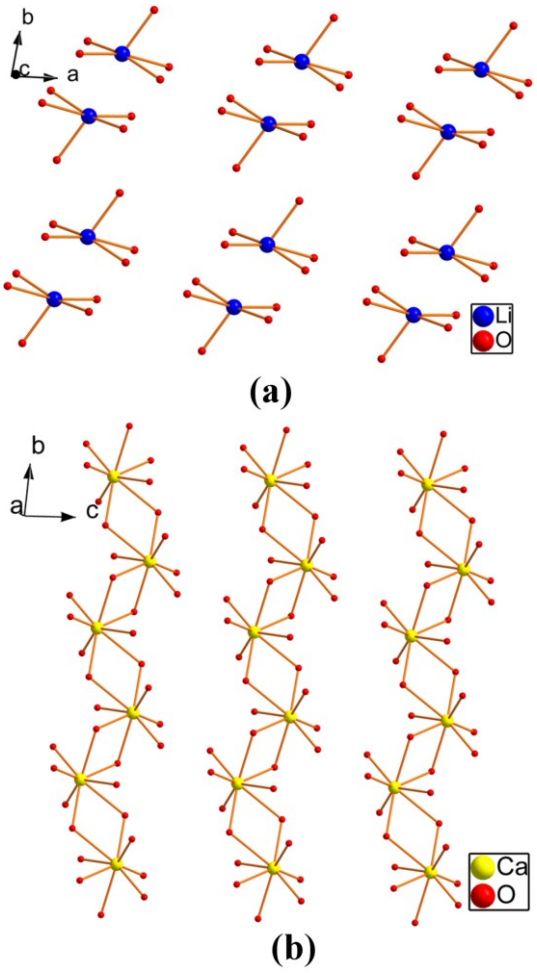


Fig. S5. (a) The 1D $(PO_3)_\infty$ chain of $LiCa(PO_3)_3$; (b) the 1D $(PO_3)_\infty$ chain of $LiZn(PO_3)_3$.

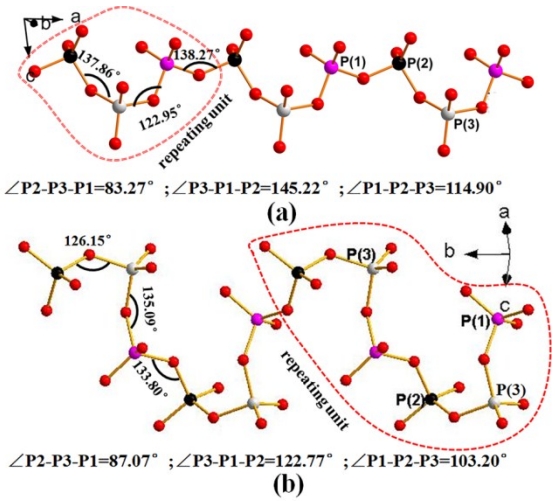


Fig. S6. The arrangement of ZnO_6 in $LiZn(PO_3)_3$.

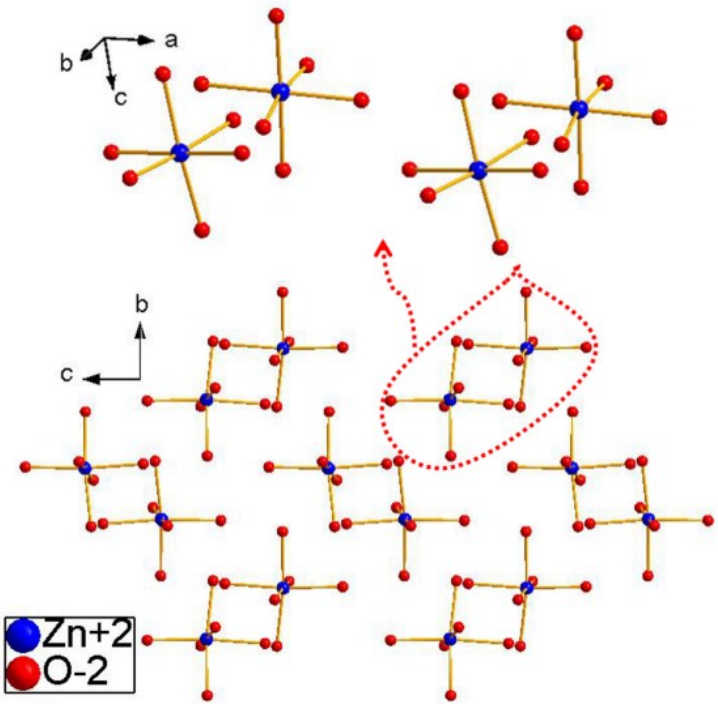


Fig. S7. The arrangement of P-O chains in $LiZn(PO_3)_3$

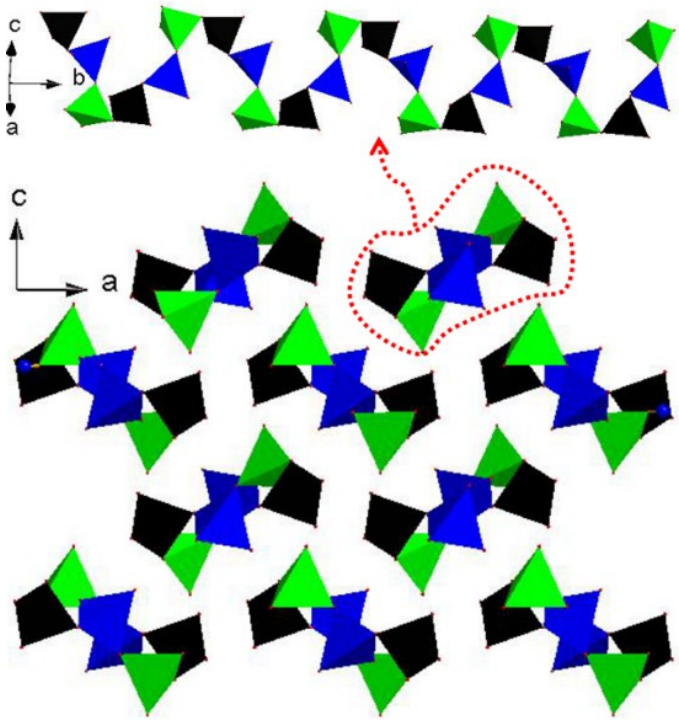
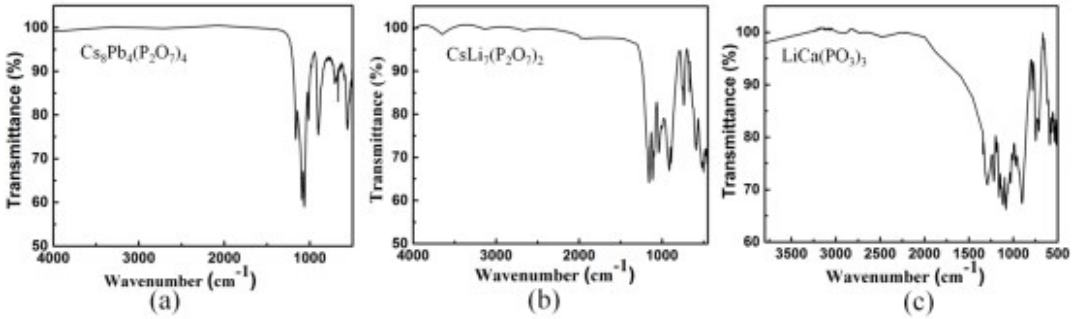


Fig. S8. The IR spectra of the three compounds.



References

(1) M. T. Averbuch-Pouchot, *Z. Anorg. Allg. Chem*., 1985, **529**, 143.

(2) S. S. Huang, Q. Jing, J. Han, S. L. Pan, H. P. Wu, Z. H. Yang, *Eur. J. Inorg. Chem*., 2015, **9**, 1490.

(3) M. Abudoureheman, S. J. Han, X. Y. Dong, B. H. Lei, Y. Wang, Z. H. Yang, X. F. Long, S. L. Pan, *J. Alloy Compd*., 2017, **690**, 330.

(4) N. El-Horr, M. Bagieu, *Acta Crystallogr. C*, 1987, **43**, 603.

(5) L. Li, Y. Wang, B. H. Lei, S. J. Han, Z. H. Yang, K. R. Poeppelmeier, S. L. Pan, *J. Am. Chem. Soc*., 2016, **138**, 9101.

(6) Y. G. Shen, Y. Yang, S. G. Zhao, B. Q. Zhao, Z. S. Lin, C. M. Ji, L. N. Li, P. Fu, M. C. Hong, J. H. Luo, *Chem. Mater*., 2016, **28**, 7110.

(7) X. Y. Cheng, M. H. Whangbo, G. C. Guo, M. C. Hong, S. Q. Deng, *Angew. Chem. Int. Ed*., 2018, **57**, 3933.

(8) P. Lightfoot, M. C. Pienkowski, P. G. Bruce, I. Abrahams, *J. Mater. Chem*., 1991, **1**, 1061.

(9) M. Y. Chen, Z. G. Xia, M. S. Molokeev, T. Wang, Q. L. Liu, *Chem. Mater*., 2017, **29**, 1430.

(10) V. A. Morozov, V. A. Belik, R. N. Kotov, I. A. Presniakov, S. S. Khasanov, B. I. Lazoryak, *Kristallogr*., 2000, **45**, 19.