Electronic Supplementary Material (ESI) for Dalton Transactions.

Three New Phosphates with Isolated P_2O_7 unit: Noncentrosymmetric $Cs_2Ba_3(P_2O_7)_2$ and Centrosymmetric $Cs_2BaP_2O_7$, $LiCsBaP_2O_7$

Lin Li,[a,b] Shujuan Han,[*a] Bing-Hua Lei,[a,b] Ying Wang,[a] Hongyi Li,[a] Zhihua Yang,[a] and Shilie Pan[*a]

[a]*Key Laboratory of Functional Materials and Devices for Special Environments of CAS;*

Xinjiang Key Laboratory of Electronic Information Materials and Devices;

Xinjiang Technical Institute of Physics & Chemistry of CAS, 40-1 South Beijing Road, Urumqi 830011, China.

[b]*University of Chinese Academy of Sciences, Beijing 100049, China.*

To whom correspondence should be addressed.

E-mail: slpan@ms.xjb.ac.cn (Shilie Pan); hansj@ms.xjb.ac.cn (Shujuan Han)

Phone: (+86)991-3674558, Fax: (+86)991-3838957

Table S1a. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Cs_2Ba_3(P_2O_7)_2$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Ba1	5671(1)	5264(1)	92(1)	15(1)	2.02
Ba2	4163(1)	11470(1)	1155(1)	17(1)	2.07
Ba3	7515(1)	8338(1)	1630(1)	15(1)	1.92
Cs1	2675(1)	6683(1)	1696(1)	27(1)	0.98
Cs2	827(1)	8083(1)	3717(1)	21(1)	1.13
P1	2122(2)	4076(1)	55(1)	13(1)	4.92
P2	4807(2)	8733(2)	-101(1)	13(1)	4.96
P3	1192(2)	10441(2)	2056(1)	13(1)	4.95
P4	3967(2)	9589(2)	2859(1)	15(1)	4.97
O1	8544(4)	5246(4)	7(3)	24(1)	2.13
O2	3321(4)	3882(4)	616(3)	24(1)	2.03
O3	2750(5)	4612(4)	-643(2)	28(1)	1.92
O4	4533(5)	7639(4)	-676(3)	23(1)	2.17
O5	6158(4)	9661(4)	-409(2)	15(1)	2.25
O6	5327(5)	8072(5)	587(2)	26(1)	1.87
O7	5076(5)	9829(5)	2265(2)	26(1)	1.91
O8	4128(5)	8170(4)	3200(3)	36(1)	2.03
O9	3859(5)	10754(5)	3397(2)	26(1)	1.91
O10	2344(4)	9441(4)	2481(2)	23(1)	2.34
O11	1437(5)	10076(5)	1271(2)	26(1)	1.99
O12	1747(5)	11913(4)	2197(2)	24(1)	1.97
O13	-329(5)	10085(5)	2318(3)	29(1)	1.84
O14	1149(4)	2807(4)	-41(3)	23(1)	1.91

Table S1b. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Cs_2BaP_2O_7$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Cs1	3619(1)	2354(1)	8433(1)	32(1)	0.90
Cs2	6408(1)	2239(1)	6740(1)	22(1)	1.05
Ba1	7511(1)	2573(1)	9915(1)	13(1)	2.26
P1	4593(1)	7237(2)	6355(1)	13(1)	4.93
P2	9682(1)	2401(2)	6415(1)	13(1)	5.07
O1	8991(3)	291(6)	6444(3)	19(1)	2.05
O2	5975(3)	7130(6)	6310(3)	26(1)	2.07
O3	3946(3)	5050(6)	6262(3)	28(1)	2.00
O4	4610(4)	8125(7)	7447(3)	31(1)	2.20
O5	3805(4)	8937(6)	5685(3)	29(1)	1.92
O6	10777(4)	2223(7)	5935(4)	40(1)	2.00
O7	8799(4)	4260(6)	6028(3)	37(1)	1.98

Table S1c. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $LiCsBaP_2O_7$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Ba1	8067(1)	4432(1)	1226(1)	13(1)	2.13
Cs1	7497(1)	8269(1)	-40(1)	25(1)	0.87
Li1	6662(10)	2599(6)	3594(6)	18(1)	1.05
P1	3778(1)	4849(1)	1975(1)	12(1)	4.92
P2	8385(1)	1356(1)	1634(1)	12(1)	4.94
O1	6559(4)	459(2)	1726(2)	16(1)	2.17
O2	4655(4)	5857(2)	1299(2)	16(1)	1.82
O3	1818(4)	4419(2)	1115(2)	17(1)	1.99
O4	8804(4)	2211(2)	2799(2)	18(1)	1.85
O5	5208(4)	3806(2)	2447(3)	19(1)	1.96
O6	7582(4)	2062(2)	389(2)	18(1)	1.85
O7	10055(4)	502(2)	1612(3)	20(1)	2.06

Table S2a. Selected bond lengths [Å] and angles [deg] for $Cs_2Ba_3(P_2O_7)_2$

Ba(1)-O(1)	2.596(4)	Cs(2)-O(5)#13	3.251(4)
Ba(1)-O(11)#1	2.658(5)	Cs(2)-O(13)	3.408(5)
Ba(1)-O(2)	2.685(4)	Cs(2)-O(13)#10	3.498(5)
Ba(1)-O(6)	2.869(5)	Cs(2)-O(11)#10	3.538(5)
Ba(1)-O(4)	2.884(5)	P(1)-O(3)	1.512(4)
Ba(1)-O(9)#2	2.894(5)	P(1)-O(14)	1.512(4)
Ba(1)-O(14)#3	2.983(4)	P(1)-O(2)	1.517(4)
Ba(1)-O(3)	3.035(5)	P(1)-O(5)#8	1.633(4)
Ba(2)-O(8)#6	2.549(4)	P(2)-O(6)	1.509(4)
Ba(2)-O(2)#7	2.639(4)	P(2)-O(1)#8	1.513(4)
Ba(2)-O(7)	2.731(5)	P(2)-O(4)	1.523(4)
Ba(2)-O(1)#8	2.783(5)	P(2)-O(5)	1.615(4)
Ba(2)-O(11)	2.807(5)	P(3)-O(13)	1.496(5)
Ba(2)-O(14)#1	2.834(5)	P(3)-O(12)	1.522(4)
Ba(2)-O(12)	2.952(5)	P(3)-O(11)	1.524(5)
Ba(3)-O(12)#2	2.668(5)	P(3)-O(10)	1.623(4)
Ba(3)-O(3)#1	2.708(4)	P(4)-O(9)	1.508(5)
Ba(3)-O(4)#1	2.715(4)	P(4)-O(8)	1.511(4)
Ba(3)-O(9)#2	2.775(5)	P(4)-O(7)	1.512(5)
Ba(3)-O(6)	2.786(4)	P(4)-O(10)	1.631(4)
Ba(3)-O(13)#9	2.872(5)	O(2)-Ba(1)-O(3)	51.55(13)
Ba(3)-O(7)	2.880(5)	O(6)-Ba(1)-O(3)	104.23(12)
Cs(1)-O(10)	3.043(4)	O(4)-Ba(1)-O(3)	68.26(11)
Cs(1)-O(5)#8	3.054(4)	O(10)-Cs(1)-O(6)	91.20(12)
Cs(1)-O(13)#10	3.198(5)	O(5)#8-Cs(1)-O(6)	90.03(11)
Cs(1)-O(9)#2	3.255(5)	O(1)-Ba(1)-O(9)#2	85.08(14)
Cs(1)-O(7)#2	3.324(5)	O(8)-Cs(1)-O(6)	93.85(12)
Cs(1)-O(8)	3.413(5)	O(2)-Cs(1)-O(6)	80.23(11)
Cs(1)-O(2)	3.414(5)	O(8)-Cs(1)-O(11)	85.44(10)
Cs(1)-O(6)	3.434(5)	O(2)-Cs(1)-O(11)	130.34(11)
Cs(1)-O(4)#8	3.477(5)	O(6)-Cs(1)-O(11)	74.10(11)
Cs(1)-O(11)	3.536(5)	O(4)#8-Cs(1)-O(11)	56.41(10)
Cs(2)-O(10)	2.984(5)	O(3)-P(1)-O(14)	113.0(3)
Cs(2)-O(14)#11	3.061(5)	O(3)-P(1)-O(2)	111.7(3)
Cs(2)-O(12)#10	3.093(4)	O(14)-P(1)-O(2)	113.3(2)
Cs(2)-O(3)#12	3.129(5)	O(3)-P(1)-O(5)#8	107.2(2)
Cs(2)-O(8)	3.130(6)	O(14)-P(1)-O(5)#8	109.8(2)
Cs(2)-O(1)#6	3.213(5)	O(2)-P(1)-O(5)#8	101.0(2)

Symmetry transformations used to generate equivalent atoms:

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

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

#9 -x+1, -y+5/2, z-1/2 #10 x, y+1/2, z+1/2 #11 x,y+1/2,z-1/2 #12 -x+1,-y+5/2,z+1/2

#13 x, y+1/2, z+3/2 #14 x, y-1/2, z+1/2

Table S2b. Selected bond lengths [Å] and angles [deg] for $Cs_2BaP_2O_7$

Cs(1)-O(1)#1	3.116(4)	Cs(2)-O(5)#3	3.464(4)
Cs(1)-O(6)#1	3.155(5)	Cs(2)-O(4)#3	3.488(5)
Cs(1)-O(3)#2	3.230(4)	Ba(1)-O(6)#6	2.623(4)
Cs(1)-O(4)#3	3.256(4)	Ba(1)-O(7)#4	2.631(4)
Cs(1)-O(7)#4	3.293(4)	Ba(1)-O(5)#7	2.637(4)
Cs(1)-O(5)#2	3.305(4)	Ba(1)-O(3)#8	2.644(4)
Cs(1)-O(6)#4	3.309(4)	Ba(1)-O(2)#4	2.657(4)
Cs(1)-O(4)#2	3.400(4)	Ba(1)-O(1)#1	2.718(3)
Cs(1)-O(3)	3.539(4)	P(1)-O(2)	1.506(4)
Cs(2)-O(3)	3.091(4)	P(1)-O(5)	1.507(4)
Cs(2)-O(2)	3.094(4)	P(1)-O(3)	1.510(4)
Cs(2)-O(1)	3.152(3)	P(1)-O(4)	1.607(4)
Cs(2)-O(2)#3	3.225(4)	P(2)-O(7)	1.498(4)
Cs(2)-O(7)	3.239(4)	P(2)-O(6)	1.501(4)
Cs(2)-O(1)#1	3.263(4)	P(2)-O(1)	1.508(4)
Cs(2)-O(2)#4	3.354(4)	P(2)-O(4)#4	1.624(4)
Cs(2)-O(5)#5	3.390(4)		
O(6)#1-Cs(1)-O(6)#4	146.02(17)	O(6)#6-Ba(1)-O(7)#4	86.62(15)
O(3)#2-Cs(1)-O(6)#4	69.99(10)	O(6)#6-Ba(1)-O(5)#7	96.70(13)
O(5)#2-Cs(1)-O(6)#4	107.76(10)	O(7)#4-Ba(1)-O(5)#7	174.39(13)
O(1)#1-Cs(1)-O(4)#2	133.52(9)	O(6)#6-Ba(1)-O(3)#8	90.82(13)
O(6)#1-Cs(1)-O(4)#2	94.72(11)	O(7)#4-Ba(1)-O(3)#8	90.61(13)
O(3)#2-Cs(1)-O(4)#2	44.06(9)	O(5)#7-Ba(1)-O(3)#8	93.86(12)
O(4)#3-Cs(1)-O(4)#2	112.22(11)	O(7)#4-Ba(1)-O(1)#1	89.62(12)
O(3)-Cs(2)-O(5)#3	71.86(9)	O(5)#7-Ba(1)-O(1)#1	85.97(12)
O(2)-Cs(2)-O(5)#3	115.50(9)	O(2)-P(1)-O(4)	106.6(2)
O(1)-Cs(2)-O(5)#3	111.25(9)	O(5)-P(1)-O(4)	102.0(2)
O(2)#3-Cs(2)-O(5)#3	44.22(9)	O(3)-P(1)-O(4)	106.1(2)
O(7)-Cs(2)-O(5)#3	135.83(11)	O(7)-P(2)-O(6)	113.3(3)
O(5)#5-Cs(2)-O(5)#3	67.54(11)	O(7)-P(2)-O(1)	113.7(2)
O(3)-Cs(2)-O(4)#3	87.90(10)	O(6)-P(2)-O(1)	113.5(2)
O(2)-Cs(2)-O(4)#3	134.47(9)	O(7)-P(2)-O(4)#4	103.2(3)
O(1)-Cs(2)-O(4)#3	109.32(9)	O(6)-P(2)-O(4)#4	103.2(3)

Symmetry transformations used to generate equivalent atoms:

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

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

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

#10 -x+1, -y+1, -z+2 #11 -x+1/2, y+1/2, -z+3/2 #12 x, y+1, z

#13 x+1/2, -y+1/2, z-1/2 #14 x-1/2, -y+1/2, z-1/2 #15 x-1/2, -y+3/2, z-1/2

Table S2c. Selected bond lengths [Å] and angles [deg] for $LiCsBaP_2O_7$

Ba(1)-O(7)#1	2.611(3)	O(5)-Ba(1)-O(2)	52.79(7)
Ba(1)-O(3)#2	2.690(3)	O(3)#3-Ba(1)-O(2)	90.74(7)
Ba(1)-O(6)	2.709(3)	O(7)#1-Ba(1)-O(2)#3	158.79(8)
Ba(1)-O(5)	2.773(3)	O(2)-Ba(1)-O(2)#3	74.39(8)
Ba(1)-O(3)#3	2.820(3)	O(7)#1-Ba(1)-O(4)	83.28(8)
Ba(1)-O(2)	2.884(3)	O(3)#2-Ba(1)-O(4)	89.77(8)
Ba(1)-O(2)#3	2.885(3)	O(6)-Ba(1)-O(4)	52.73(7)
Ba(1)-O(4)	2.902(3)	O(5)-Ba(1)-O(4)	64.13(8)
Cs(1)-O(7)#5	3.030(3)	O(3)#3-Ba(1)-O(4)	146.96(7)
Cs(1)-O(1)#6	3.212(3)	O(2)-Ba(1)-O(4)	116.64(7)
Cs(1)-O(3)#3	3.213(3)	O(2)#3-Ba(1)-O(4)	115.15(7)
Cs(1)-O(7)#6	3.244(3)	O(7)#5-Cs(1)-O(1)#6	104.07(7)
Cs(1)-O(4)#1	3.247(3)	O(7)#5-Cs(1)-O(3)#3	91.98(7)
Cs(1)-O(1)#3	3.258(3)	O(1)#6-Cs(1)-O(3)#3	162.62(7)
Cs(1)-O(6)#3	3.531(3)	O(7)#5-Cs(1)-O(7)#6	69.96(8)
Cs(1)-O(5)#3	3.564(3)	O(1)#6-Cs(1)-O(7)#6	45.76(7)
Cs(1)-O(6)#5	3.620(3)	O(3)#3-Cs(1)-O(7)#6	138.95(7)
Li(1)-O(6)#8	1.893(7)	O(7)#5-Cs(1)-O(4)#1	95.61(7)
Li(1)-O(5)	1.896(7)	O(1)#6-Cs(1)-O(4)#1	94.49(6)
Li(1)-O(4)	1.973(7)	O(3)#3-Cs(1)-O(4)#1	77.07(6)
Li(1)-O(2)#9	2.120(7)	O(7)#6-Cs(1)-O(4)#1	68.85(7)
P(1)-O(5)	1.510(3)	O(7)#5-Cs(1)-O(1)#3	93.25(7)
P(1)-O(3)	1.517(3)	O(1)#6-Cs(1)-O(1)#3	73.96(7)
P(1)-O(2)	1.531(3)	O(3)#3-Cs(1)-O(1)#3	112.30(6)
P(1)-O(1)#7	1.614(3)	O(5)-P(1)-O(3)	113.24(16)
P(2)-O(7)	1.506(3)	O(5)-P(1)-O(2)	111.73(15)
P(2)-O(6)	1.509(3)	O(3)-P(1)-O(2)	110.63(15)
P(2)-O(4)	1.518(3)	O(5)-P(1)-O(1)#7	105.00(15)
P(2)-O(1)	1.640(3)	O(3)-P(1)-O(1)#7	109.04(15)
O(7)#1-Ba(1)-O(3)#2	76.63(8)	O(2)-P(1)-O(1)#7	106.81(14)
O(3)#2-Ba(1)-O(6)	91.08(8)	O(7)-P(2)-O(4)	114.01(16)
O(7)#1-Ba(1)-O(5)	87.24(8)	O(6)-P(2)-O(4)	111.23(15)
O(6)-Ba(1)-O(5)	83.17(8)	O(6)-P(2)-O(1)	103.73(15)
O(3)#2-Ba(1)-O(3)#3	72.42(9)	O(6)#8-Li(1)-O(5)	120.2(4)
O(6)-Ba(1)-O(3)#3	98.91(7)	O(6)#8-Li(1)-O(4)	112.7(4)
O(5)-Ba(1)-O(3)#3	136.60(8)	O(5)-Li(1)-O(4)	102.3(3)
O(7)#1-Ba(1)-O(2)	88.21(8)	O(6)#8-Li(1)-O(2)#9	98.8(3)
O(6)-Ba(1)-O(2)	118.89(8)	O(4)-Li(1)-O(2)#9	103.5(3)

Symmetry transformations used to generate equivalent atoms:

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

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

#9 -x+1, -y+5/2, z-1/2 #10 x, y+1/2, z+1/2 #11 x,y+1/2,z-1/2 #12 -x+1,-y+5/2,z+1/2

#13 x, y+1/2, z+3/2 #14 x, y-1/2, z+1/2

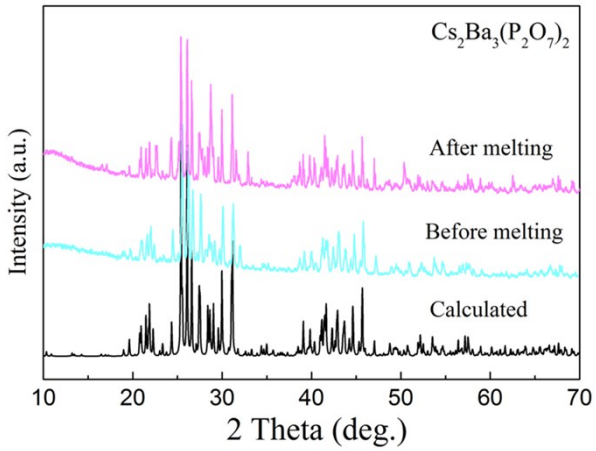


Figure S1a. Experimental and calculated XRD patterns of $Cs_2Ba_3(P_2O_7)_2$.

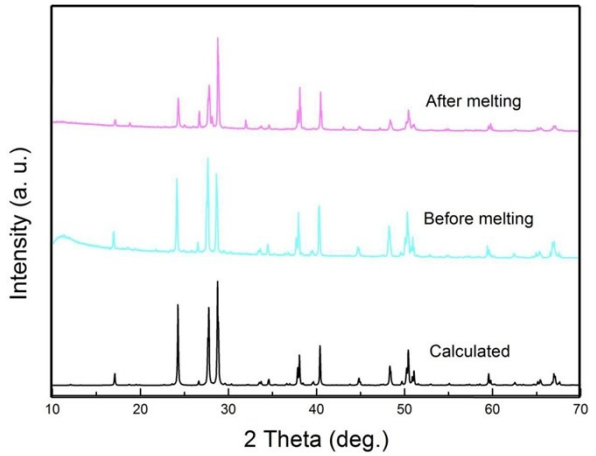


Figure S1b. Experimental and calculated XRD patterns of $Cs_2BaP_2O_7$.

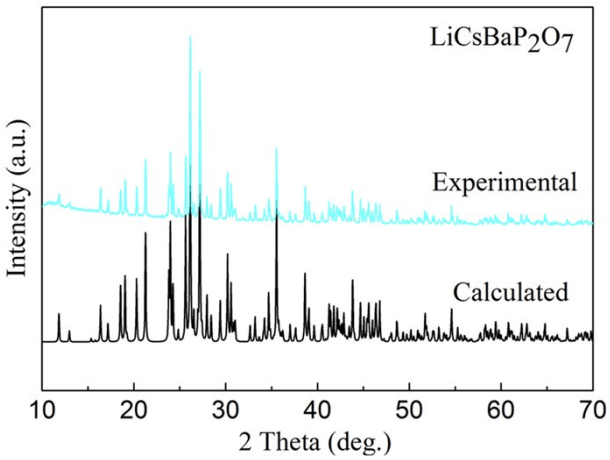


Figure S1c. Experimental and calculated XRD patterns of $LiCsBaP_2O_7$.

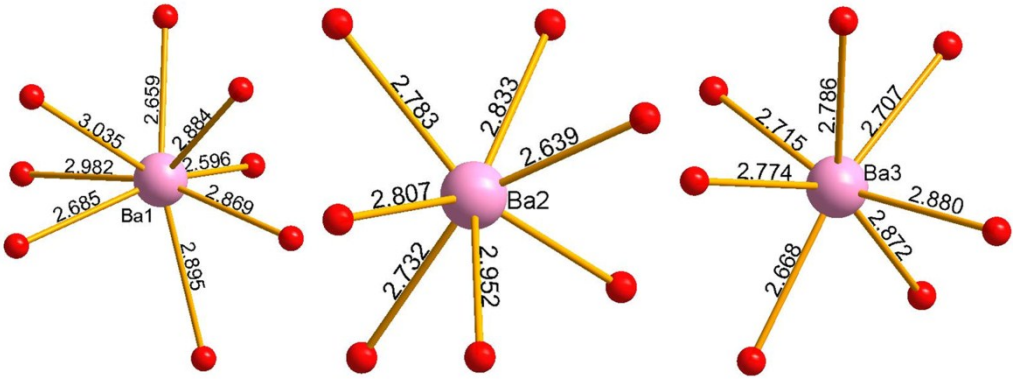


Figure S2a. Coordination environment of the Ba atoms in $Cs_2Ba_3(P_2O_7)_2$.

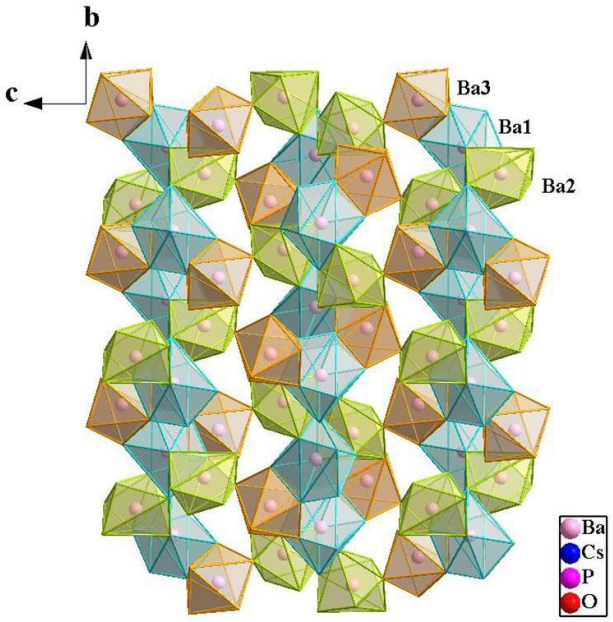


Figure S2b. The 3D network of $Cs_2Ba_3(P_2O_7)_2$ build by BaO_n (n = 7,8).

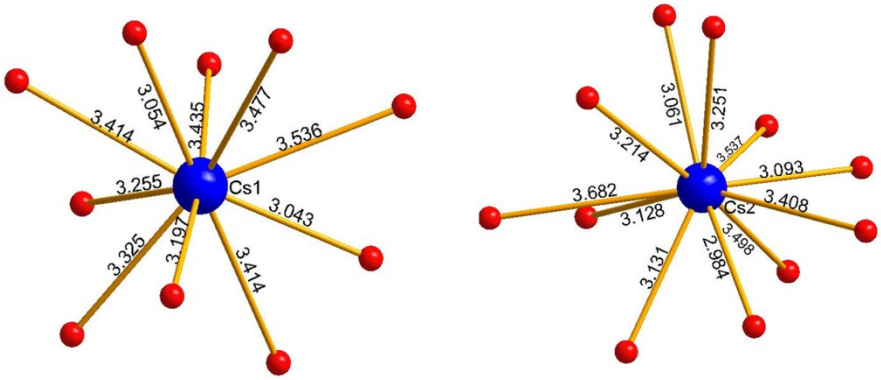


Figure S3. Coordination environment of the Cs atoms in $Cs_2Ba_3(P_2O_7)_2$.

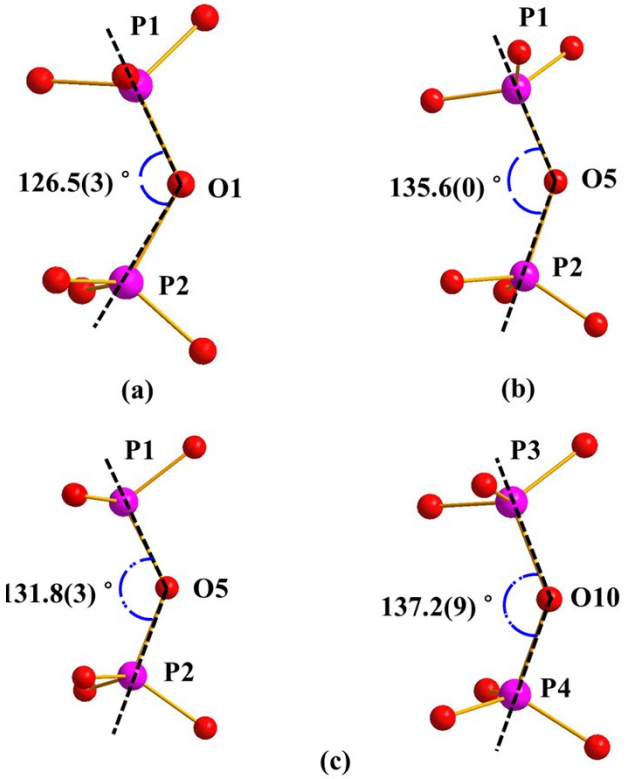


Figure S4. The P_2O_7 unit of (a) $LiCsBaP_2O_7$, (b) $Cs_2BaP_2O_7$ and (c) $Cs_2Ba_3(P_2O_7)_2$.

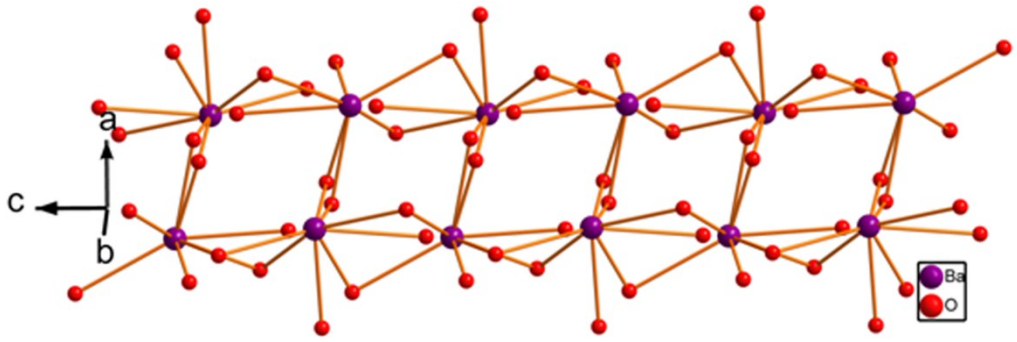
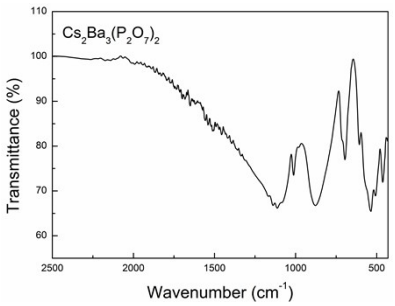
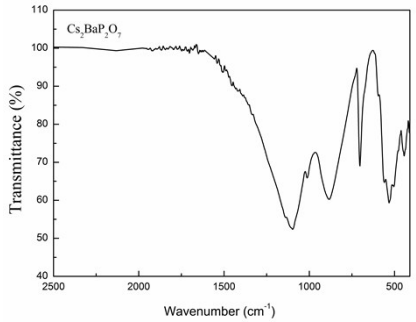


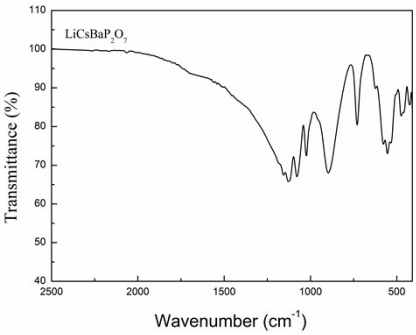
Figure S5. The 1D chain formed by the BaO_8 polyhedra in $Li_2BaP_2O_7$.



(a)



(b)



(c)

Figure S6. IR spectra of (a) $Cs_2Ba_3(P_2O_7)_2$; (b) $Cs_2BaP_2O_7$; (c) $LiCsBaP_2O_7$.

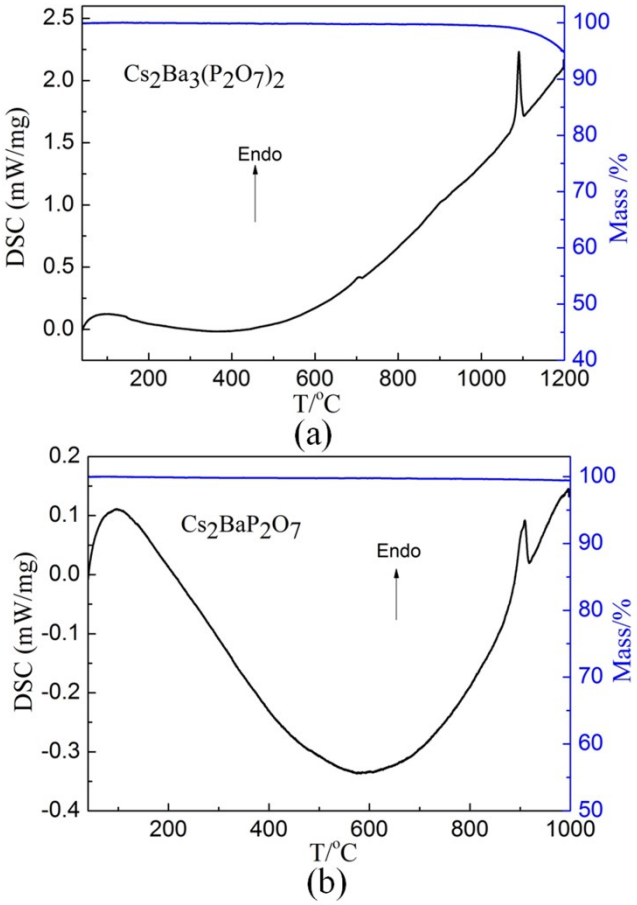


Figure S7. DSC-TG curves of $Cs_2Ba_3(P_2O_7)_2$ and $Cs_2BaP_2O_7$.