Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Syntheses, structures and characterization of non-centrosymmetric $Rb_2Zn_3(P_2O_7)_2$ and centrosymmetric $Cs_2M_3(P_2O_7)_2$ (M= Zn, Mg)

Zhongfu Song,[1] Hongwei Yu,[1] Hongping Wu,*[1] Zhanggui Hu,[1] Jiyang Wang,[1] Yicheng Wu[1]

[1]*Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystal, Tianjin University of Technology, Tianjin 300384, China.*

To whom correspondence should be addressed:wuhp@ms.xjb.ac.cn.

CONTENTS

Table S1(a). Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_2Zn_3(P_2O_7)_2$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Rb(1)	0.44683(9)	0.87890(9)	0.41697(5)	0.02234(15)	1.03
Rb(2)	0.88898(9)	0.12121(10)	0.09426(5)	0.02308(15)	0.94
Zn(1)	0.70864(9)	0.62822(10)	0.09790(5)	0.01161(15)	2.14
Zn(2)	0.29206(10)	0.24808(9)	0.26322(5)	0.01199(15)	2.04
Zn(3)	0.95159(10)	0.71784(10)	0.38728(5)	0.01441(16)	2.16
P(1)	0.3883(2)	0.9042(2)	0.10793(11)	0.0099(3)	5.08
P(2)	0.6649(2)	0.4161(2)	0.31040(11)	0.0115(3)	5.09
P(3)	0.1352(2)	0.6135(2)	0.18340(10)	0.0099(3)	5.06
P(4)	0.9333(2)	0.1413(2)	0.38834(11)	0.0114(3)	5.12
O(1)	0.5862(5)	0.8657(6)	0.0792(3)	0.0180(9)	2.05
O(2)	0.1565(6)	0.4072(6)	0.1682(3)	0.0155(9)	2.01
O(3)	0.9698(6)	0.6943(6)	0.1252(3)	0.0177(10)	2.02
O(4)	0.3122(5)	0.6997(6)	0.1316(3)	0.0130(9)	2.14
O(5)	0.1356(5)	0.1389(7)	0.3653(3)	0.0217(10)	2.03
O(6)	0.5029(6)	0.3143(6)	0.3542(3)	0.0158(9)	2.01
O(7)	0.6269(6)	0.4651(7)	0.2010(3)	0.0247(11)	1.97
O(8)	0.7230(6)	0.5754(6)	0.3782(4)	0.0225(11)	2.06
O(9)	0.8381(6)	0.2782(6)	0.3058(3)	0.0164(10)	2.20
O(10)	0.1465(6)	0.6668(6)	0.2940(3)	0.0200(10)	1.98
O(11)	0.8933(6)	0.2187(8)	0.4907(3)	0.0327(13)	2.05
O(12)	0.8391(6)	0.9581(7)	0.3677(5)	0.0369(14)	2.04
O(13)	0.2657(6)	0.9755(6)	0.0212(3)	0.0210(10)	2.06
O(14)	0.3765(7)	0.0176(6)	0.2018(4)	0.0293(12)	2.03

Table S1(b). Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Cs_2Zn_3(P_2O_7)_2$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Cs(1)	8999(1)	159(1)	8232(1)	23(1)	1.09
Cs(2)	5936(1)	2535(1)	10276(1)	29(1)	0.92
Zn(1)	7437(1)	-1450(1)	6289(1)	14(1)	2.19
Zn(2)	6147(1)	716(1)	12668(1)	16(1)	2.25
Zn(3)	11057(1)	126(1)	6161(1)	13(1)	2.23
P(1)	8899(1)	1916(2)	5713(1)	13(1)	5.13
P(2)	11757(1)	-38(2)	8205(1)	13(1)	5.08
P(3)	6079(1)	-60(2)	8052(1)	14(1)	5.23
P(4)	6817(1)	-2952(2)	9249(1)	14(1)	5.10
O(1)	11222(4)	-866(6)	7391(3)	17(1)	2.10
O(2)	12854(4)	-374(7)	8244(3)	22(1)	2.08
O(3)	11510(4)	1934(6)	8326(3)	16(1)	2.00
O(4)	6589(4)	-3034(6)	10251(3)	22(1)	2.05
O(5)	6559(4)	-904(6)	8974(3)	22(1)	2.20
O(6)	8696(3)	4023(6)	5899(3)	14(1)	2.10
O(7)	6125(4)	-4191(6)	8720(3)	23(1)	2.06
O(8)	8038(4)	907(6)	6079(4)	24(1)	2.10
O(9)	8973(4)	1847(6)	4683(3)	26(1)	2.08
O(10)	7901(4)	-3163(7)	9049(4)	26(1)	2.08
O(11)	9861(4)	1493(7)	6214(4)	27(1)	2.13
O(12)	6333(5)	1902(6)	8181(4)	34(2)	2.03
O(13)	4993(4)	-447(7)	8113(4)	31(1)	2.14
O(14)	6550(5)	-932(7)	7260(4)	40(2)	2.06

Table S1(c). Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Cs_2Mg_3(P_2O_7)_2$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Cs(1)	3930(1)	517(1)	7929(1)	26(1)	0.95
Cs(2)	963(1)	-1971(1)	5864(1)	31(1)	0.94
Mg(1)	4019(2)	2547(3)	5394(2)	13(1)	2.16
Mg(2)	1193(2)	-6840(3)	6760(2)	15(1)	2.17
Mg(3)	2486(2)	-3840(3)	8743(2)	15(1)	2.13
P(1)	3888(1)	-1833(3)	5551(1)	14(1)	5.17
P(2)	1761(2)	2595(3)	9629(1)	14(1)	5.05
P(3)	1116(1)	-123(3)	8253(1)	13(1)	5.26
P(4)	6709(1)	376(3)	8075(1)	13(1)	5.21
O(1)	3067(4)	-2005(8)	4868(4)	31(1)	2.08
O(2)	1146(4)	935(7)	9198(3)	18(1)	2.22
O(3)	4090(4)	90(7)	5826(4)	20(1)	2.07
O(4)	2857(4)	2084(8)	9639(4)	23(1)	2.01
O(5)	1540(4)	4250(7)	9056(4)	20(1)	1.96
O(6)	1799(4)	-1729(7)	8345(4)	26(1)	2.04
O(7)	6067(4)	-1012(7)	8516(3)	18(1)	2.15
O(8)	6525(4)	2317(7)	8520(3)	19(1)	2.25
O(9)	1495(4)	1166(7)	7545(3)	18(1)	2.06
O(10)	6445(5)	650(8)	7092(3)	28(1)	1.96
O(11)	57(4)	-605(8)	8099(4)	29(1)	2.13
O(12)	1296(4)	2817(8)	10548(3)	23(1)	2.04
O(13)	4809(4)	-2909(8)	5315(4)	27(1)	1.99
O(14)	7810(4)	32(8)	8186(4)	28(1)	2.09

Table S2(a). Selected bond distances (Å) and angles (degrees) for $Rb_2Zn_3(P_2O_7)_2$.

Rb(1)-O(12)	2.975(5)	Rb(1)-O(5)	2.982(4)
Rb(1)-O(11)	3.006(5)	Rb(1)-O(8)	3.015(5)
Rb(1)-O(14)	3.038(5)	Rb(1)-O(10)	3.066(4)
Rb(1)-O(6)	3.067(4)	Rb(1)-O(6)	3.280(4)
Rb(1)-O(8)	3.328(5)	Rb(2)-O(7)	3.451(5)
Rb(2)-O(1)	2.856(4)	Rb(2)-O(2)	2.964(4)
Rb(2)-O(9)	3.051(4)	Rb(2)-O(13)	3.095(5)
Rb(2)-O(3)	3.152(4)	Rb(2)-O(13)	3.160(5)
Rb(2)-O(3)	3.161(4)	Rb(2)-O(4)	3.317(4)
Zn(1)-O(7)	1.910(5)	Zn(1)-O(13)	1.936(4)
Zn(1)-O(1)	1.939(4)	Zn(1)-O(3)	1.959(4)
Zn(2)-O(2)	1.938(4)	Zn(2)-O(5)	1.954(4)
Zn(2)-O(14)	1.958(5)	Zn(2)-O(6)	1.960(4)
Zn(3)-O(11)	1.927(4)	Zn(3)-O(12)	1.928(5)
Zn(3)-O(10)	1.936(4)	Zn(3)-O(8)	1.940(4)
P(1)-O(14)	1.492(5)	P(1)-O(13)	1.510(4)
P(1)-O(1)	1.513(4)	P(1)-O(4)	1.610(4)
P(2)-O(7)	1.503(4)	P(2)-O(8)	1.507(4)
P(2)-O(6)	1.511(4)	P(2)-O(9)	1.598(4)
P(3)-O(10)	1.510(4)	P(3)-O(3)	1.510(4)
P(3)-O(2)	1.512(4)	P(3)-O(4)	1.594(4)
P(4)-O(5)	1.498(4)	P(4)-O(11)	1.500(5)
P(4)-O(12)	1.507(5)	P(4)-O(9)	1.606(4)
O(12)-Rb(1)-O(5)	122.63(13)	O(12)-Rb(1)-O(11)	162.91(14)
O(5)-Rb(1)-O(11)	73.71(14)	O(12)-Rb(1)-O(8)	57.73(13)
O(5)-Rb(1)-O(8)	155.90(12)	O(11)-Rb(1)-O(8)	109.93(15)
O(12)-Rb(1)-O(14)	81.86(15)	O(5)-Rb(1)-O(14)	58.71(12)
O(11)-Rb(1)-O(14)	113.38(14)	O(8)-Rb(1)-O(14)	99.71(13)
O(12)-Rb(1)-O(10)	129.48(14)	O(5)-Rb(1)-O(10)	71.61(13)
O(11)-Rb(1)-O(10)	56.94(12)	O(8)-Rb(1)-O(10)	90.16(11)
O(14)-Rb(1)-O(10)	65.10(13)	O(12)-Rb(1)-O(6)	99.59(14)
O(5)-Rb(1)-O(6)	112.43(12)	O(11)-Rb(1)-O(6)	67.01(11)
O(8)-Rb(1)-O(6)	90.15(12)	O(14)-Rb(1)-O(6)	169.02(12)
O(10)-Rb(1)-O(6)	120.12(12)	O(12)-Rb(1)-O(6)	68.53(12)
O(5)-Rb(1)-O(6)	55.74(12)	O(11)-Rb(1)-O(6)	125.52(14)
O(8)-Rb(1)-O(6)	124.46(12)	O(14)-Rb(1)-O(6)	57.68(11)
O(10)-Rb(1)-O(6)	115.83(11)	O(6)-Rb(1)-O(6)	112.56(11)
O(12)-Rb(1)-O(8)	118.41(14)	O(5)-Rb(1)-O(8)	67.83(11)
O(11)-Rb(1)-O(8)	60.33(12)	O(8)-Rb(1)-O(8)	135.41(8)
O(14)-Rb(1)-O(8)	124.53(12)	O(10)-Rb(1)-O(8)	111.80(11)
O(6)-Rb(1)-O(8)	45.30(10)	O(6)-Rb(1)-O(8)	81.33(11)
O(1)-Rb(2)-O(2)	163.22(12)	O(1)-Rb(2)-O(9)	100.76(12)
O(2)-Rb(2)-O(9)	62.46(11)	O(1)-Rb(2)-O(13)	115.68(12)

O(2)-Rb(2)-O(13)	76.94(12)	O(9)-Rb(2)-O(13)	123.24(11)
O(1)-Rb(2)-O(3)	108.36(12)	O(2)-Rb(2)-O(3)	87.66(11)
O(9)-Rb(2)-O(3)	146.54(11)	O(13)-Rb(2)-O(3)	56.92(11)
O(1)-Rb(2)-O(13)	103.60(11)	O(2)-Rb(2)-O(13)	78.93(11)
O(9)-Rb(2)-O(13)	95.13(11)	O(13)-Rb(2)-O(13)	114.94(9)
O(3)-Rb(2)-O(13)	62.63(11)	O(1)-Rb(2)-O(3)	61.00(11)
O(2)-Rb(2)-O(3)	121.52(11)	O(9)-Rb(2)-O(3)	105.77(11)
O(13)-Rb(2)-O(3)	63.24(12)	O(3)-Rb(2)-O(3)	102.60(11)
O(13)-Rb(2)-O(3)	155.75(10)	O(1)-Rb(2)-O(4)	75.01(11)
O(2)-Rb(2)-O(4)	115.72(10)	O(9)-Rb(2)-O(4)	134.25(10)
O(13)-Rb(2)-O(4)	97.79(10)	O(3)-Rb(2)-O(4)	44.65(10)
O(13)-Rb(2)-O(4)	45.02(10)	O(3)-Rb(2)-O(4)	110.79(10)
O(1)-Rb(2)-O(7)	93.80(12)	O(2)-Rb(2)-O(7)	73.86(11)
O(9)-Rb(2)-O(7)	43.31(10)	O(13)-Rb(2)-O(7)	150.48(12)
O(3)-Rb(2)-O(7)	117.07(11)	O(13)-Rb(2)-O(7)	55.01(11)
O(3)-Rb(2)-O(7)	138.57(11)	O(4)-Rb(2)-O(7)	91.03(10)
O(7)-Zn(1)-O(13)	105.6(2)	O(7)-Zn(1)-O(1)	119.0(2)
O(13)-Zn(1)-O(1)	117.16(19)	O(7)-Zn(1)-O(3)	109.73(18)
O(13)-Zn(1)-O(3)	99.71(18)	O(1)-Zn(1)-O(3)	103.67(18)
O(14)-Zn(2)-O(6)	102.50(19)	O(2)-Zn(2)-O(5)	113.40(17)
O(2)-Zn(2)-O(14)	113.1(2)	O(5)-Zn(2)-O(14)	98.0(2)
O(2)-Zn(2)-O(6)	127.74(17)	O(5)-Zn(2)-O(6)	97.34(18)
O(11)-Zn(3)-O(12)	109.7(2)	O(11)-Zn(3)-O(10)	97.06(19)
O(12)-Zn(3)-O(10)	113.3(2)	O(11)-Zn(3)-O(8)	121.1(2)
O(12)-Zn(3)-O(8)	96.8(2)	O(10)-Zn(3)-O(8)	119.44(19)
O(1)-P(1)-O(4)	102.1(2)	O(14)-P(1)-O(13)	113.3(3)
O(14)-P(1)-O(1)	113.1(3)	O(13)-P(1)-O(1)	113.6(3)
O(14)-P(1)-O(4)	108.2(3)	O(13)-P(1)-O(4)	105.5(2)
O(7)-P(2)-O(8)	115.4(3)	O(7)-P(2)-O(6)	111.5(2)
O(8)-P(2)-O(6)	110.2(3)	O(7)-P(2)-O(9)	103.0(3)
O(8)-P(2)-O(9)	107.4(2)	O(6)-P(2)-O(9)	109.0(2)
O(2)-P(3)-O(4)	104.0(2)	O(10)-P(3)-O(3)	114.1(2)
O(10)-P(3)-O(2)	112.2(2)	O(3)-P(3)-O(2)	113.3(2)
O(10)-P(3)-O(4)	107.5(2)	O(3)-P(3)-O(4)	104.9(2)
O(12)-P(4)-O(9)	103.8(3)	O(5)-P(4)-O(11)	114.1(3)
O(5)-P(4)-O(12)	112.8(3)	O(11)-P(4)-O(12)	112.9(3)
O(5)-P(4)-O(9)	105.2(2)	O(11)-P(4)-O(9)	106.9(3)

Table S2(b). Selected bond distances (Å) and angles (degrees) for $Cs_2Zn_3(P_2O_7)_2$.

Cs(1)-O(9)#1	3.069(5)	P(3)-O(12)	1.504(5)
Cs(1)-O(1)#2	3.094(4)	P(3)-O(5)	1.607(5)
Cs(1)-O(10)	3.120(5)	P(4)-O(10)	1.501(5)
Cs(1)-O(11)#3	3.214(5)	P(4)-O(4)	1.502(5)
Cs(1)-O(11)	3.339(5)	P(4)-O(7)	1.510(5)
Cs(1)-O(1)	3.344(5)	P(4)-O(5)	1.605(5)
Cs(1)-O(3)#3	3.360(4)	O(9)#1-Cs(1)-O(1)#2	60.84(12)
Cs(1)-O(8)	3.419(6)	O(9)#1-Cs(1)-O(10)	107.05(13)
Cs(1)-O(6)#3	3.432(5)	O(1)#2-Cs(1)-O(10)	145.07(13)
Cs(1)-O(5)	3.566(5)	O(9)#1-Cs(1)-O(11)#3	116.66(14)
Cs(1)-O(3)	3.626(5)	O(1)#2-Cs(1)-O(11)#3	156.97(13)
Cs(1)-O(14)	3.650(7)	O(10)-Cs(1)-O(11)#3	57.62(13)
Cs(2)-O(13)#4	3.100(5)	O(9)#1-Cs(1)-O(11)	113.89(13)
Cs(2)-O(2)#5	3.121(5)	O(1)#2-Cs(1)-O(11)	59.48(12)
Cs(2)-O(12)	3.152(6)	O(10)-Cs(1)-O(11)	138.35(13)
Cs(2)-O(8)#1	3.250(5)	O(11)#3-Cs(1)-O(11)	107.43(10)
Cs(2)-O(5)	3.298(5)	O(9)#1-Cs(1)-O(1)	116.15(13)
Cs(2)-O(7)#6	3.338(5)	O(1)#2-Cs(1)-O(1)	100.90(10)
Cs(2)-O(7)#4	3.393(5)	O(10)-Cs(1)-O(1)	113.30(12)
Cs(2)-O(4)#6	3.398(5)	O(11)#3-Cs(1)-O(1)	58.33(12)
Cs(2)-O(4)#4	3.487(5)	O(11)-Cs(1)-O(1)	54.06(12)
Zn(1)-O(14)	1.912(5)	O(9)#1-Cs(1)-O(3)#3	167.60(13)
Zn(1)-O(4)#7	1.917(5)	O(1)#2-Cs(1)-O(3)#3	117.45(12)
Zn(1)-O(3)#3	1.929(5)	O(10)-Cs(1)-O(3)#3	66.86(13)
Zn(1)-O(8)	1.951(5)	O(11)#3-Cs(1)-O(3)#3	70.08(12)
Zn(2)-O(13)#4	1.902(6)	O(11)-Cs(1)-O(3)#3	71.49(12)
Zn(2)-O(7)#9	1.908(5)	O(1)-Cs(1)-O(3)#3	76.18(11)
Zn(2)-O(2)#5	1.928(5)	O(9)#1-Cs(1)-O(8)	120.57(12)
Zn(2)-O(12)#1	1.932(5)	O(1)#2-Cs(1)-O(8)	62.85(11)
Zn(3)-O(11)	1.905(5)	O(10)-Cs(1)-O(8)	107.88(13)
Zn(3)-O(9)#10	1.912(5)	O(11)#3-Cs(1)-O(8)	122.54(12)
Zn(3)-O(10)#2	1.919(5)	O(11)-Cs(1)-O(8)	43.31(12)
Zn(3)-O(1)	1.948(5)	O(1)-Cs(1)-O(8)	91.32(12)
P(1)-O(8)	1.487(5)	O(3)#3-Cs(1)-O(8)	54.89(11)
P(1)-O(11)	1.506(5)	O(9)#1-Cs(1)-O(6)#3	86.84(13)
P(1)-O(9)	1.510(5)	O(1)#2-Cs(1)-O(6)#3	114.98(12)
P(1)-O(6)	1.608(4)	O(10)-Cs(1)-O(6)#3	95.52(12)
P(2)-O(2)	1.496(5)	O(11)#3-Cs(1)-O(6)#3	43.67(11)
P(2)-O(1)	1.508(5)	O(11)-Cs(1)-O(6)#3	94.05(12)
P(2)-O(3)	1.509(4)	O(1)-Cs(1)-O(6)#3	43.25(11)
P(2)-O(6)#3	1.612(4)	O(3)#3-Cs(1)-O(6)#3	104.23(11)
P(3)-O(14)	1.478(5)	O(8)-Cs(1)-O(6)#3	134.52(11)
P(3)-O(13)	1.493(5)	O(9)#1-Cs(1)-O(5)	85.74(13)

O(1)#2-Cs(1)-O(5)	102.49(12)	O(13)#4-Cs(2)-O(7)#4	60.43(13)
O(10)-Cs(1)-O(5)	42.57(11)	O(2)#5-Cs(2)-O(7)#4	107.79(12)
O(11)#3-Cs(1)-O(5)	100.04(12)	O(12)-Cs(2)-O(7)#4	129.04(14)
O(11)-Cs(1)-O(5)	132.29(12)	O(8)#1-Cs(2)-O(7)#4	115.37(12)
O(1)-Cs(1)-O(5)	153.83(11)	O(5)-Cs(2)-O(7)#4	138.46(12)
O(3)#3-Cs(1)-O(5)	82.71(11)	O(7)#6-Cs(2)-O(7)#4	96.10(11)
O(8)-Cs(1)-O(5)	89.01(12)	O(13)#4-Cs(2)-O(4)#6	126.76(13)
O(6)#3-Cs(1)-O(5)	131.60(11)	O(2)#5-Cs(2)-O(4)#6	111.82(13)
O(9)#1-Cs(1)-O(3)	74.67(12)	O(12)-Cs(2)-O(4)#6	94.82(12)
O(1)#2-Cs(1)-O(3)	75.50(11)	O(8)#1-Cs(2)-O(4)#6	55.78(12)
O(10)-Cs(1)-O(3)	136.00(12)	O(5)-Cs(2)-O(4)#6	132.13(12)
O(11)#3-Cs(1)-O(3)	81.79(11)	O(7)#6-Cs(2)-O(4)#6	42.89(12)
O(11)-Cs(1)-O(3)	65.51(12)	O(7)#4-Cs(2)-O(4)#6	82.49(11)
O(1)-Cs(1)-O(3)	41.95(10)	O(13)#4-Cs(2)-O(4)#4	79.30(13)
O(3)#3-Cs(1)-O(3)	117.40(8)	O(2)#5-Cs(2)-O(4)#4	134.37(12)
O(8)-Cs(1)-O(3)	108.09(11)	O(12)-Cs(2)-O(4)#4	89.17(14)
O(6)#3-Cs(1)-O(3)	40.56(10)	O(8)#1-Cs(2)-O(4)#4	151.42(11)
O(5)-Cs(1)-O(3)	158.66(11)	O(5)-Cs(2)-O(4)#4	102.29(12)
O(9)#1-Cs(1)-O(14)	113.91(13)	O(7)#6-Cs(2)-O(4)#4	81.97(12)
O(1)#2-Cs(1)-O(14)	90.95(13)	O(7)#4-Cs(2)-O(4)#4	41.93(12)
O(10)-Cs(1)-O(14)	62.84(14)	O(4)#6-Cs(2)-O(4)#4	98.40(11)
O(11)#3-Cs(1)-O(14)	109.45(13)	O(13)#4-Cs(2)-O(5)#4	40.60(12)
O(11)-Cs(1)-O(14)	92.89(13)	O(2)#5-Cs(2)-O(5)#4	95.16(12)
O(1)-Cs(1)-O(14)	127.89(11)	O(12)-Cs(2)-O(5)#4	113.97(13)
O(3)#3-Cs(1)-O(14)	53.84(11)	O(8)#1-Cs(2)-O(5)#4	141.82(12)
O(8)-Cs(1)-O(14)	50.05(11)	O(5)-Cs(2)-O(5)#4	99.17(11)
O(6)#3-Cs(1)-O(14)	152.99(11)	O(7)#6-Cs(2)-O(5)#4	120.94(12)
O(5)-Cs(1)-O(14)	40.56(12)	O(7)#4-Cs(2)-O(5)#4	41.09(11)
O(3)-Cs(1)-O(14)	158.13(11)	O(4)#6-Cs(2)-O(5)#4	123.18(11)
O(13)#4-Cs(2)-O(2)#5	55.34(13)	O(4)#4-Cs(2)-O(5)#4	39.23(11)
O(13)#4-Cs(2)-O(12)	137.87(14)	Zn(2)-Cs(2)-O(5)#4	70.33(8)
O(2)#5-Cs(2)-O(12)	119.96(13)	O(14)-Zn(1)-O(4)#7	104.8(3)
O(13)#4-Cs(2)-O(8)#1	105.36(14)	O(14)-Zn(1)-O(3)#3	112.0(2)
O(2)#5-Cs(2)-O(8)#1	59.66(12)	O(4)#7-Zn(1)-O(3)#3	121.8(2)
O(12)-Cs(2)-O(8)#1	103.82(14)	O(14)-Zn(1)-O(8)	101.8(2)
O(13)#4-Cs(2)-O(5)	99.43(14)	O(4)#7-Zn(1)-O(8)	107.2(2)
O(2)#5-Cs(2)-O(5)	82.41(13)	O(3)#3-Zn(1)-O(8)	107.3(2)
O(12)-Cs(2)-O(5)	43.53(12)	O(13)#4-Zn(2)-O(7)#9	113.2(2)
O(8)#1-Cs(2)-O(5)	104.62(12)	O(13)#4-Zn(2)-O(2)#5	97.9(2)
O(13)#4-Cs(2)-O(7)#6	156.51(13)	O(7)#9-Zn(2)-O(2)#5	120.1(2)
O(2)#5-Cs(2)-O(7)#6	142.97(13)	O(13)#4-Zn(2)-O(12)#1	115.1(2)
O(12)-Cs(2)-O(7)#6	55.25(12)	O(7)#9-Zn(2)-O(12)#1	103.4(2)
O(8)#1-Cs(2)-O(7)#6	84.80(13)	O(2)#5-Zn(2)-O(12)#1	107.6(2)
O(5)-Cs(2)-O(7)#6	98.31(12)	O(11)-Zn(3)-O(9)#10	115.2(2)

O(11)-Zn(3)-O(10)#2	106.0(2)	O(1)-P(2)-O(3)	112.6(3)
O(9)#10-Zn(3)-O(10)#2	114.0(2)	O(2)-P(2)-O(6)#3	106.7(3)
O(11)-Zn(3)-O(1)	104.1(2)	O(1)-P(2)-O(6)#3	106.4(3)
O(9)#10-Zn(3)-O(1)	107.9(2)	O(3)-P(2)-O(6)#3	103.6(2)
O(10)#2-Zn(3)-O(1)	109.1(2)	O(14)-P(3)-O(13)	113.5(4)
O(8)-P(1)-O(11)	112.9(3)	O(14)-P(3)-O(12)	114.8(3)
O(8)-P(1)-O(9)	114.1(3)	O(13)-P(3)-O(12)	113.4(3)
O(11)-P(1)-O(9)	113.7(3)	O(14)-P(3)-O(5)	108.3(3)
O(8)-P(1)-O(6)	106.9(3)	O(13)-P(3)-O(5)	104.6(3)
O(11)-P(1)-O(6)	105.5(3)	O(12)-P(3)-O(5)	100.6(3)
O(9)-P(1)-O(6)	102.5(3)	O(10)-P(4)-O(4)	113.9(3)
O(10)-P(4)-O(5)	104.8(3)	O(10)-P(4)-O(7)	115.4(3)
O(4)-P(4)-O(5)	103.6(3)	O(4)-P(4)-O(7)	109.7(3)
O(2)-P(2)-O(1)	114.6(3)	O(7)-P(4)-O(5)	108.6(3)
O(2)-P(2)-O(3)	112.0(3)		

Symmetry transformations used to generate equivalent atoms:

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

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

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

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

#10 -x+2,-y,-z+1 #11 x,y-1,z

Table S2(c). Selected bond distances (Å) and angles (degrees) for $Cs_2Mg_3(P_2O_7)_2$.

Cs(1)-O(3)	3.132(5)	P(3)-O(11)	1.474(6)
Cs(1)-O(4)	3.138(5)	P(3)-O(6)	1.497(5)
Cs(1)-O(7)	3.178(5)	P(3)-O(9)	1.503(5)
Cs(1)-O(8)#1	3.234(5)	P(3)-O(2)	1.598(5)
Cs(1)-O(13)#2	3.286(6)	P(4)-O(7)	1.488(5)
Cs(1)-O(7)#2	3.327(5)	P(4)-O(14)	1.499(6)
Cs(1)-O(9)	3.329(5)	P(4)-O(10)	1.504(6)
Cs(1)-O(6)	3.353(6)	P(4)-O(8)	1.592(5)
Cs(1)-O(10)	3.594(6)	O(3)-Cs(1)-O(4)	150.74(14)
Cs(1)-O(10)#1	3.615(6)	O(3)-Cs(1)-O(7)	99.39(14)
Cs(2)-O(14)#1	3.076(6)	O(4)-Cs(1)-O(8)#1	135.72(13)
Cs(2)-O(12)#3	3.123(6)	O(7)-Cs(1)-O(8)#1	94.81(13)
Cs(2)-O(1)	3.188(6)	O(3)-Cs(1)-O(13)#2	141.04(14)
Cs(2)-O(2)#4	3.210(5)	O(4)-Cs(1)-O(13)#2	57.99(14)
Cs(2)-O(11)#4	3.376(6)	O(7)-Cs(1)-O(13)#2	57.27(14)
Cs(2)-O(5)#3	3.432(6)	O(8)#1-Cs(1)-O(13)#2	150.36(14)
Cs(2)-O(9)	3.457(5)	O(3)-Cs(1)-O(7)#2	55.99(13)
Cs(2)-O(5)#4	3.464(5)	O(4)-Cs(1)-O(7)#2	103.78(14)
Cs(2)-O(8)#1	3.506(6)	O(7)-Cs(1)-O(7)#2	116.00(10)
Cs(2)-O(12)#4	3.650(6)	O(8)#1-Cs(1)-O(7)#2	97.82(13)
Cs(2)-O(11)	3.669(6)	O(13)#2-Cs(1)-O(7)#2	103.36(14)
Mg(1)-O(13)#5	1.912(6)	O(3)-Cs(1)-O(9)	85.64(13)
Mg(1)-O(3)	1.919(6)	O(4)-Cs(1)-O(9)	68.26(13)
Mg(1)-O(4)#3	1.920(6)	O(7)-Cs(1)-O(9)	165.79(13)
Mg(1)-O(7)#2	1.933(6)	O(8)#1-Cs(1)-O(9)	79.43(13)
Mg(2)-O(9)#6	1.910(6)	O(13)#2-Cs(1)-O(9)	125.04(14)
Mg(2)-O(11)#4	1.913(6)	O(7)#2-Cs(1)-O(9)	77.86(13)
Mg(2)-O(14)#1	1.917(6)	O(3)-Cs(1)-O(6)	101.57(14)
Mg(2)-O(12)#7	1.935(6)	O(4)-Cs(1)-O(6)	68.70(14)
Mg(3)-O(6)	1.893(6)	O(7)-Cs(1)-O(6)	122.47(13)
Mg(3)-O(1)#8	1.929(6)	O(8)#1-Cs(1)-O(6)	67.02(13)
Mg(3)-O(10)#1	1.935(6)	O(13)#2-Cs(1)-O(6)	117.19(14)
Mg(3)-O(5)#6	1.948(6)	O(7)#2-Cs(1)-O(6)	120.21(13)
P(1)-O(1)	1.485(6)	O(9)-Cs(1)-O(6)	43.32(12)
P(1)-O(3)	1.496(5)	O(3)-Cs(1)-O(10)	65.56(13)
P(1)-O(13)	1.507(6)	O(4)-Cs(1)-O(10)	134.79(13)
P(1)-O(8)#1	1.611(5)	O(7)-Cs(1)-O(10)	42.58(13)
P(2)-O(12)	1.509(5)	O(8)#1-Cs(1)-O(10)	87.77(13)
P(2)-O(5)	1.510(5)	O(13)#2-Cs(1)-O(10)	77.86(13)
P(2)-O(4)	1.511(6)	O(7)#2-Cs(1)-O(10)	75.54(13)
P(2)-O(2)	1.599(5)	O(9)-Cs(1)-O(10)	148.50(12)
O(6)-Cs(1)-O(10)	151.03(13)	O(2)#4-Cs(2)-O(5)#3	117.57(13)
O(3)-Cs(1)-O(10)#1	84.47(12)	O(11)#4-Cs(2)-O(5)#3	155.55(13)

O(4)-Cs(1)-O(10)#1	107.81(14)	O(14)#1-Cs(2)-O(9)	92.68(14)
O(7)-Cs(1)-O(10)#1	77.04(13)	O(12)#3-Cs(2)-O(9)	54.97(13)
O(8)#1-Cs(1)-O(10)#1	41.30(12)	O(1)-Cs(2)-O(9)	99.31(14)
O(13)#2-Cs(1)-O(10)#1	115.15(14)	O(2)#4-Cs(2)-O(9)	120.89(13)
O(7)#2-Cs(1)-O(10)#1	139.12(12)	O(11)#4-Cs(2)-O(9)	106.45(13)
O(9)-Cs(1)-O(10)#1	90.33(13)	O(5)#3-Cs(2)-O(9)	97.10(12)
O(6)-Cs(1)-O(10)#1	52.84(13)	O(14)#1-Cs(2)-O(5)#4	132.79(14)
O(10)-Cs(1)-O(10)#1	98.85(13)	O(12)#3-Cs(2)-O(5)#4	83.73(14)
O(3)-Cs(1)-O(8)	100.95(12)	O(1)-Cs(2)-O(5)#4	150.96(14)
O(4)-Cs(1)-O(8)	96.37(12)	O(2)#4-Cs(2)-O(5)#4	43.87(13)
O(7)-Cs(1)-O(8)	41.19(12)	O(11)#4-Cs(2)-O(5)#4	78.20(13)
O(8)#1-Cs(1)-O(8)	124.68(9)	O(5)#3-Cs(2)-O(5)#4	95.81(12)
O(13)#2-Cs(1)-O(8)	40.43(12)	O(9)-Cs(2)-O(5)#4	89.57(12)
O(7)#2-Cs(1)-O(8)	82.64(12)	O(14)#1-Cs(2)-O(8)#1	43.22(13)
O(9)-Cs(1)-O(8)	151.06(12)	O(12)#3-Cs(2)-O(8)#1	92.71(13)
O(6)-Cs(1)-O(8)	154.50(12)	O(1)-Cs(2)-O(8)#1	43.27(13)
O(10)-Cs(1)-O(8)	38.43(11)	O(2)#4-Cs(2)-O(8)#1	140.56(12)
O(10)#1-Cs(1)-O(8)	118.20(12)	O(11)#4-Cs(2)-O(8)#1	98.84(12)
O(3)-Cs(1)-O(10)#2	95.87(12)	O(5)#3-Cs(2)-O(8)#1	93.77(12)
O(4)-Cs(1)-O(10)#2	65.23(13)	O(9)-Cs(2)-O(8)#1	74.07(12)
O(7)-Cs(1)-O(10)#2	118.06(13)	O(5)#4-Cs(2)-O(8)#1	161.95(12)
O(8)#1-Cs(1)-O(10)#2	133.85(12)	O(14)#1-Cs(2)-O(12)#4	131.48(14)
O(13)#2-Cs(1)-O(10)#2	73.92(13)	O(12)#3-Cs(2)-O(12)#4	94.29(13)
O(7)#2-Cs(1)-O(10)#2	40.12(12)	O(1)-Cs(2)-O(12)#4	117.60(13)
O(9)-Cs(1)-O(10)#2	74.25(13)	O(2)#4-Cs(2)-O(12)#4	40.94(12)
O(6)-Cs(1)-O(10)#2	112.21(13)	O(11)#4-Cs(2)-O(12)#4	83.72(13)
O(10)-Cs(1)-O(10)#2	95.37(15)	O(5)#3-Cs(2)-O(12)#4	76.82(12)
O(10)#1-Cs(1)-O(10)#2	164.47(19)	O(9)-Cs(2)-O(12)#4	126.89(12)
O(8)-Cs(1)-O(10)#2	77.05(12)	O(5)#4-Cs(2)-O(12)#4	40.50(12)
O(14)#1-Cs(2)-O(12)#3	133.87(15)	O(8)#1-Cs(2)-O(12)#4	157.49(12)
O(14)#1-Cs(2)-O(1)	74.74(15)	O(14)#1-Cs(2)-O(11)	88.01(15)
O(12)#3-Cs(2)-O(1)	79.10(15)	O(12)#3-Cs(2)-O(11)	85.16(13)
O(14)#1-Cs(2)-O(2)#4	97.55(14)	O(1)-Cs(2)-O(11)	135.98(13)
O(12)#3-Cs(2)-O(2)#4	126.28(14)	O(2)#4-Cs(2)-O(11)	81.85(12)
O(1)-Cs(2)-O(2)#4	139.56(14)	O(11)#4-Cs(2)-O(11)	70.70(7)
O(14)#1-Cs(2)-O(11)#4	56.00(14)	O(5)#3-Cs(2)-O(11)	128.31(13)
O(12)#3-Cs(2)-O(11)#4	154.34(14)	O(9)-Cs(2)-O(11)	40.39(12)
O(1)-Cs(2)-O(11)#4	124.43(15)	O(5)#4-Cs(2)-O(11)	64.51(13)
O(2)#4-Cs(2)-O(11)#4	43.50(13)	O(8)#1-Cs(2)-O(11)	97.61(12)
O(14)#1-Cs(2)-O(5)#3	130.51(14)	O(12)#4-Cs(2)-O(11)	104.28(12)
O(12)#3-Cs(2)-O(5)#3	43.92(13)	O(13)#5-Mg(1)-O(3)	106.0(3)
O(1)-Cs(2)-O(5)#3	55.83(14)	O(13)#5-Mg(1)-O(4)#3	108.9(3)
O(13)#5-Mg(1)-O(7)#2	115.9(3)	O(12)-P(2)-O(5)	109.7(3)
O(3)-Mg(1)-O(4)#3	111.3(3)	O(3)-P(1)-O(8)#1	101.4(3)

O(3)-Mg(1)-O(7)#2	104.1(2)	O(12)-P(2)-O(4)	115.3(3)
O(4)#3-Mg(1)-O(7)#2	110.5(3)	O(5)-P(2)-O(4)	112.9(3)
O(9)#6-Mg(2)-O(11)#4	118.5(3)	O(12)-P(2)-O(2)	103.1(3)
O(9)#6-Mg(2)-O(14)#1	112.6(3)	O(5)-P(2)-O(2)	107.3(3)
O(11)#4-Mg(2)-O(14)#1	105.1(3)	O(4)-P(2)-O(2)	107.9(3)
O(9)#6-Mg(2)-O(12)#7	105.0(3)	O(11)-P(3)-O(6)	114.0(4)
O(11)#4-Mg(2)-O(12)#7	110.4(3)	O(11)-P(3)-O(9)	112.0(3)
O(14)#1-Mg(2)-O(12)#7	104.4(3)	O(6)-P(3)-O(9)	110.5(3)
O(6)-Mg(3)-O(1)#8	101.1(3)	O(11)-P(3)-O(2)	105.4(3)
O(6)-Mg(3)-O(10)#1	108.6(3)	O(6)-P(3)-O(2)	107.3(3)
O(1)#8-Mg(3)-O(10)#1	108.6(3)	O(9)-P(3)-O(2)	107.1(3)
O(6)-Mg(3)-O(5)#6	110.6(3)	O(7)-P(4)-O(14)	113.9(3)
O(1)#8-Mg(3)-O(5)#6	106.5(3)	O(7)-P(4)-O(10)	112.6(3)
O(10)#1-Mg(3)-O(5)#6	119.8(3)	O(14)-P(4)-O(10)	110.3(4)
O(1)-P(1)-O(3)	113.2(4)	O(7)-P(4)-O(8)	110.0(3)
O(1)-P(1)-O(13)	113.4(4)	O(14)-P(4)-O(8)	105.2(3)
O(3)-P(1)-O(13)	114.4(3)	O(10)-P(4)-O(8)	104.1(3)
O(1)-P(1)-O(8)#1	106.7(3)		

Symmetry transformations used to generate equivalent atoms:

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

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

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

#8 x,-y-1/2,z+1/2 #9 x,y+1,z #10 -x,y+1/2,-z+3/2

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

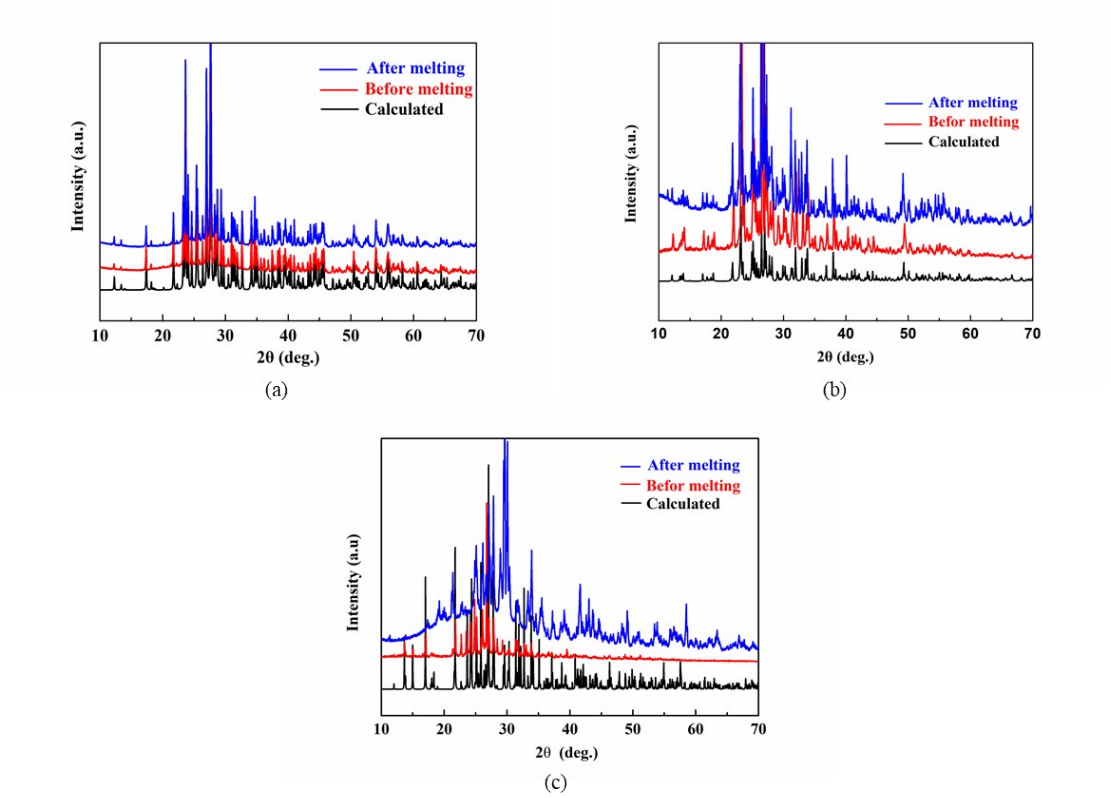

Figure S1. Powder XRD of (a) $Rb_2Zn_3(P_2O_7)_2$, (b) $Cs_2Zn_3(P_2O_7)_2$ and (c) $Cs_2Mg_3(P_2O_7)_2$.

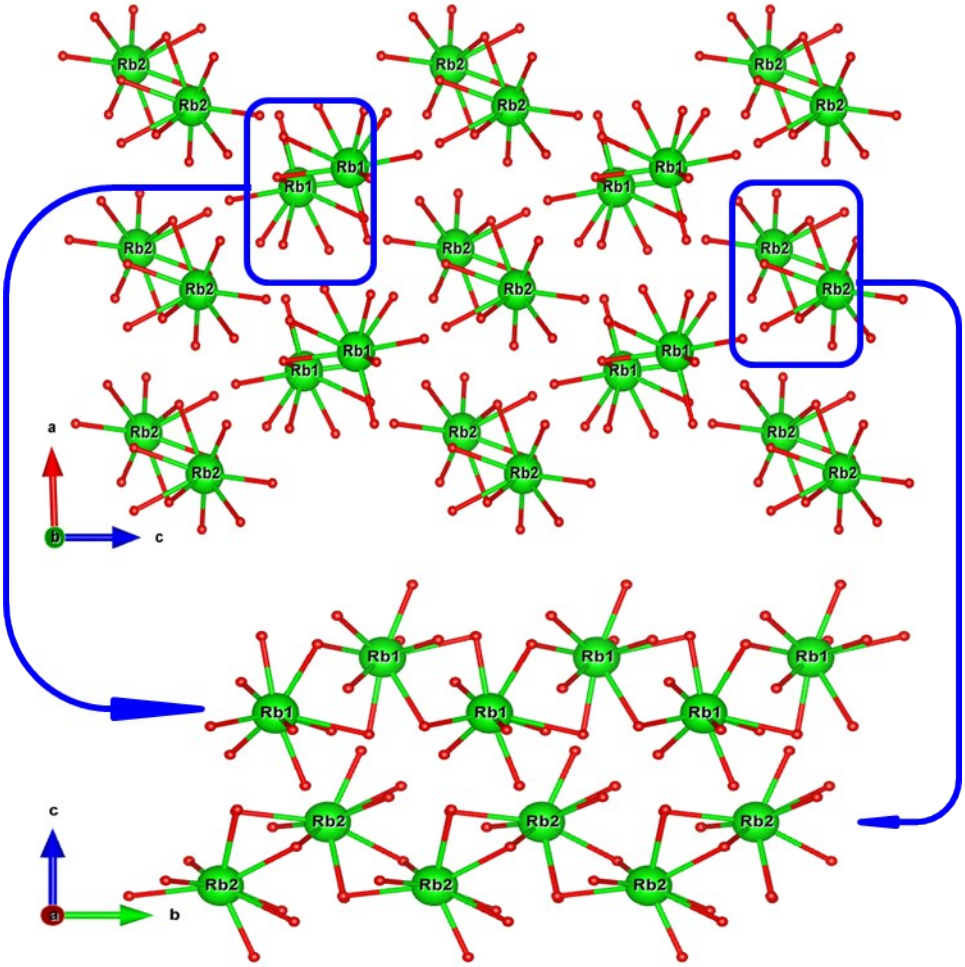

Figure S2. The $[Rb(1)O_9]_\infty$ and $[Rb(2)O_9]_\infty$ chains in $Rb_2Zn_3(P_2O_7)_2$.

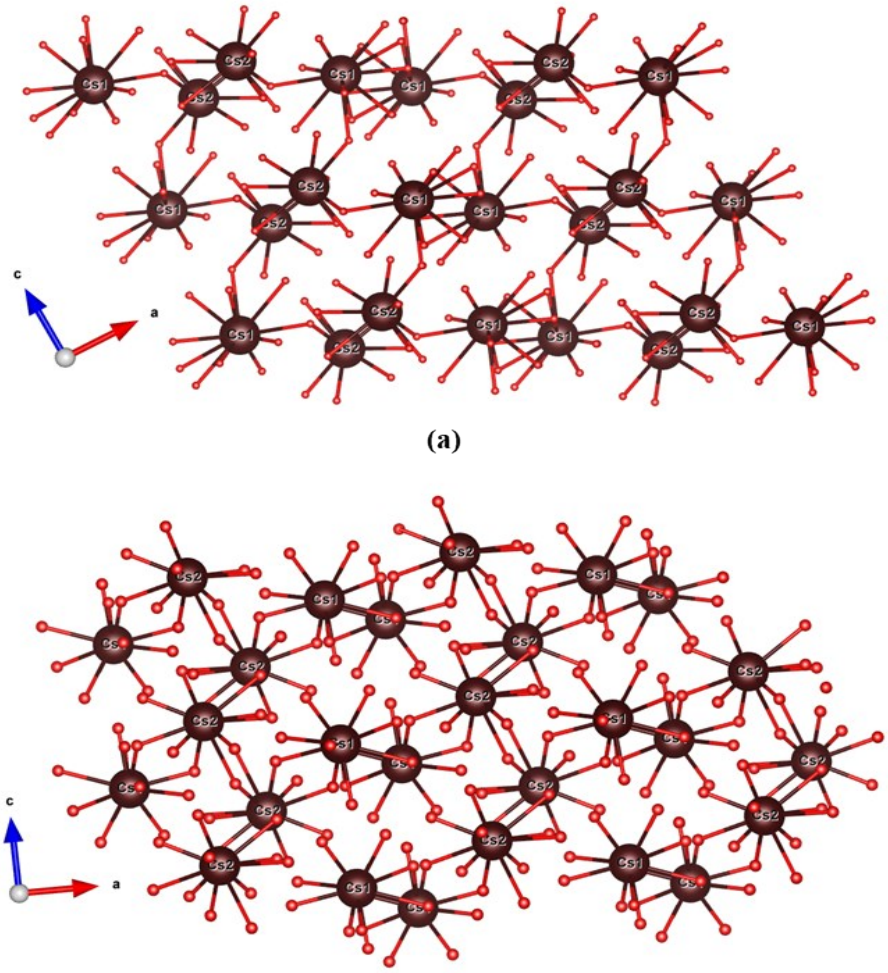

Figure S3. (a).The 3D framework composed of Cs-O polyhedra in $Cs_2Zn_3(P_2O_7)_2$; (b). The 3D framework composed of Cs-O polyhedra in $Cs_2Mg_3(P_2O_7)_2$.

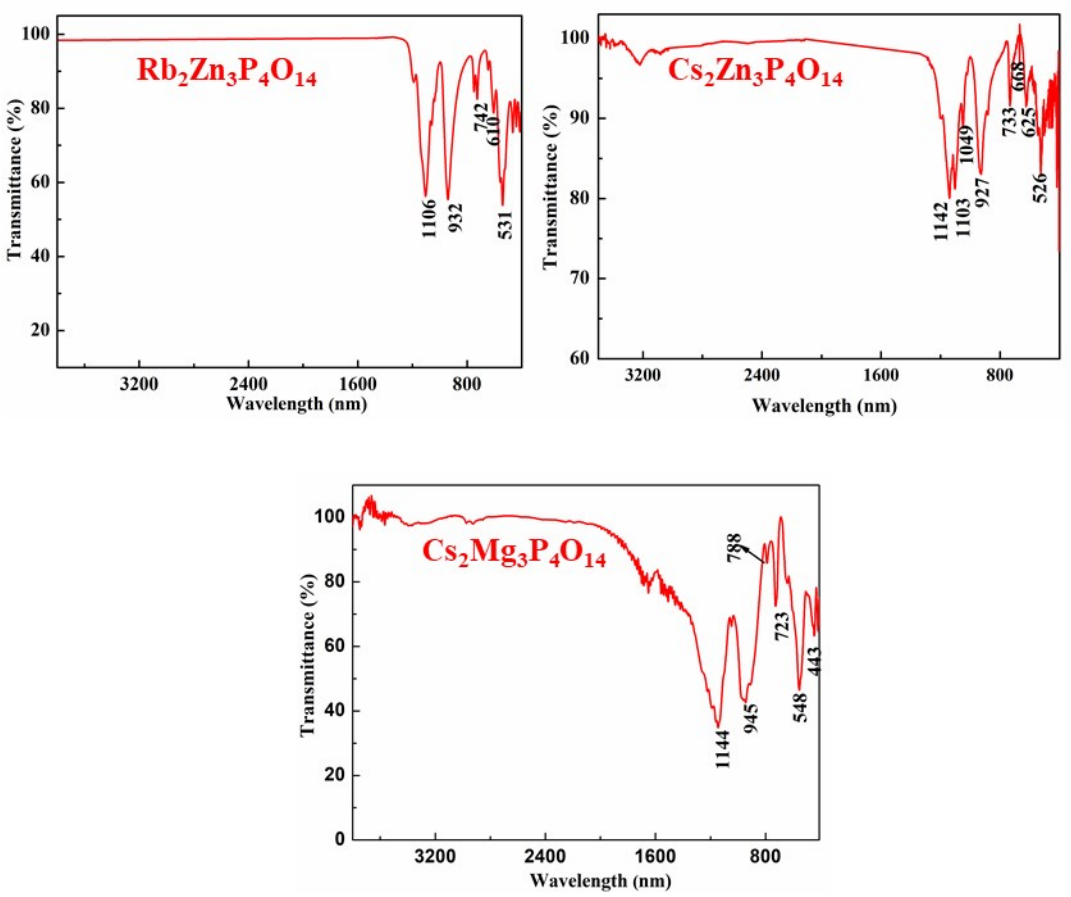

Figure S4. IR spectra of $Rb_2Zn_3(P_2O_7)_2$, $Cs_2Zn_3(P_2O_7)_2$ and $Cs_2Mg_3(P_2O_7)_2$.

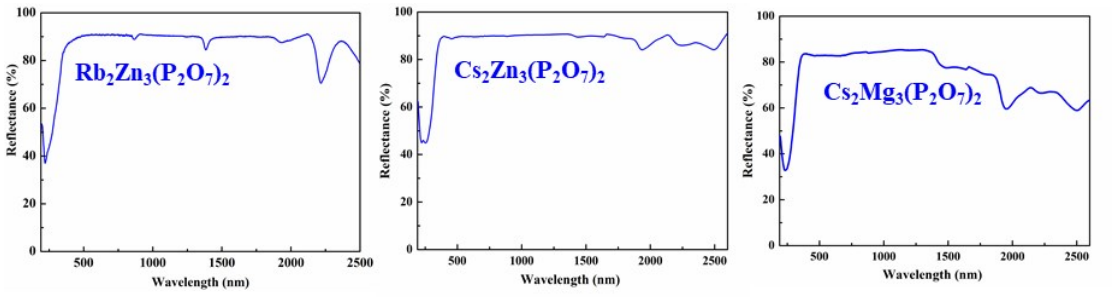

Figure S5. The UV-VIS-NIR diffuse reflectance spectra of $Rb_2Zn_3(P_2O_7)_2$, $Cs_2Zn_3(P_2O_7)_2$ and $Cs_2Mg_3(P_2O_7)_2$.

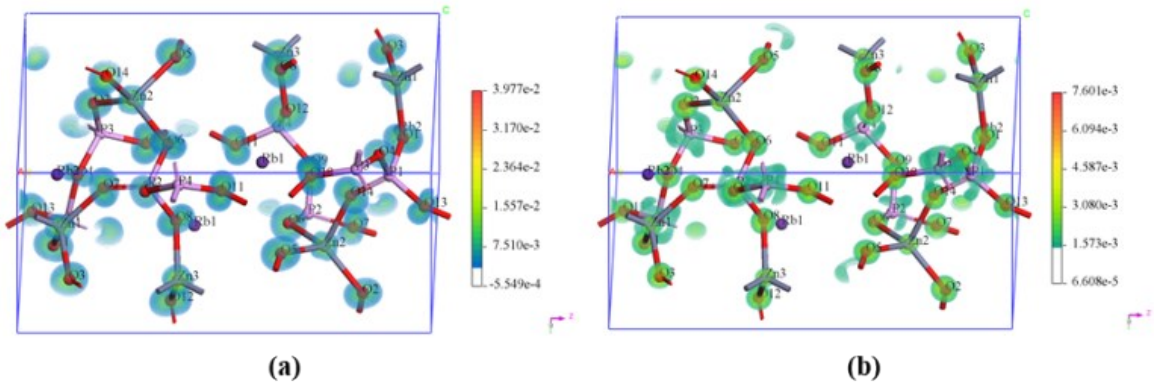

Figure S6. Virtual electron **(**VE) (a) occupied, and virtual electron (VE) (b) unoccupied orbitals of $Rb_2Zn_3(P_2O_7)_2$

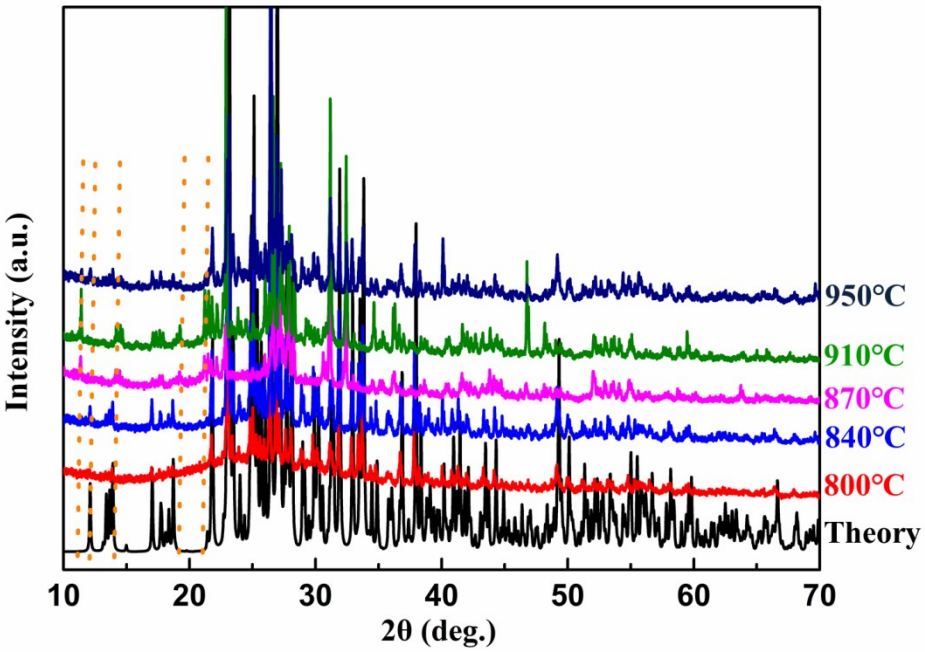

Figure S7. The Powder XRD patterns of $Cs_2Zn_3(P_2O_7)_2$ at different temperature.