# Electronic Supplementary Information

## Syntheses, Structures and Characterization of Three New Mg-containing Phosphates with Deep-UV Cut-off Edges

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**Table S1a.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $LiMg_2P_3O_{10}$. $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

| Atom | x | y | z | $U_{eq}$ | BVS |
|---|---|---|---|---|---|
| Li(1) | 0 | 0 | 5000 | 29(2) | 0.849 |
| Mg(1) | 10383(2) | 665(1) | −1656(1) | 7(1) | 2.074 |
| P(1) | 6039(2) | 2500 | 337(1) | 4(1) | 4.986 |
| P(2) | 4628(2) | 2500 | 6438(1) | 5(1) | 4.923 |
| P(3) | 3329(2) | 2500 | 3204(1) | 5(1) | 5.028 |
| O(1) | 7757(3) | 993(2) | 144(2) | 7(1) | 1.977 |
| O(2) | 2859(3) | 1006(2) | 6575(2) | 8(1) | 1.916 |
| O(3) | 2997(5) | 2500 | −577(2) | 7(1) | 1.979 |
| O(4) | 1594(3) | 996(2) | 3098(2) | 10(1) | 1.979 |
| O(5) | 7640(5) | 2500 | 7395(2) | 6(1) | 1.982 |
| O(6) | 5553(5) | 2500 | 4745(2) | 7(1) | 2.024 |
| O(7) | 5642(5) | 2500 | 2085(2) | 11(1) | 2.204 |

**Table S1b.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $CsMg_2P_3O_{10}$. $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

| Atom | x | y | z | $U_{eq}$ | BVS |
|---|---|---|---|---|---|
| Cs(1) | 5000 | 1660(1) | 2500 | 40(1) | 0.917 |
| Mg(1) | 1833(1) | 39(1) | −490(1) | 9(1) | 2.119 |
| P(1) | 0 | 1181(1) | 2500 | 9(1) | 4.967 |
| P(2) | 390(1) | 2943(1) | 774(1) | 9(1) | 4.991 |
| O(1) | 246(2) | 1512(2) | 136(2) | 13(1) | 1.999 |
| O(2) | 1082(2) | 2293(2) | 1826(1) | 12(1) | 2.009 |
| O(3) | −1225(3) | 287(2) | 1895(1) | 15(1) | 1.828 |
| O(4) | −1317(3) | 3622(2) | 982(2) | 17(1) | 1.837 |
| O(5) | 1750(3) | 4033(2) | 471(2) | 18(1) | 1.921 |

**Table S1c.** Atomic coordinates (× $10^4$) and equivalent isotropic displacement parameters (Å$^2$ × $10^3$) for $Rb_2MgP_2O_7$. $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

| Atom | x | y | z | $U_{eq}$ | BVS |
|---|---|---|---|---|---|
| Mg(1) | 3193(4) | 2500 | −1171(6) | 22(2) | 1.994 |
| Rb(1) | 831(1) | 2500 | 6519(2) | 30(1) | 0.99 |
| Rb(2) | 1223(1) | 7500 | 190(2) | 31(1) | 1.065 |
| P(1) | 2545(1) | 2500 | 2161(5) | 20(1) | 5.142 |
| P(2) | 749(3) | 2500 | 2702(5) | 20(1) | 5.169 |
| O(1) | 3076(8) | 2500 | 890(12) | 34(4) | 1.927 |
| O(2) | 863(6) | 141(13) | 3547(10) | 40(3) | 1.811 |
| O(3) | −11(9) | 2500 | 1764(16) | 56(4) | 2.081 |
| O(4) | 1564(7) | 2500 | 1607(12) | 28(3) | 2.344 |
| O(5) | 2657(5) | 96(11) | 3010(8) | 27(2) | 2.02 |

| | | | |
|---|---|---|---|
| Li(1)-O(2) | 1.9733(15) | O(4)#1-Li(1)-O(4) | 180.00(4) |
| Li(1)-O(2)#1 | 1.9733(15) | O(3)-P(1)-O(1) | 113.15(7) |
| Li(1)-O(4)#1 | 2.1207(17) | O(3)-P(1)-O(1)#8 | 113.15(7) |
| Li(1)-O(4) | 2.1207(17) | O(1)-P(1)-O(1)#8 | 113.50(12) |
| Mg(1)-O(4)#2 | 2.0260(18) | O(3)-P(1)-O(7) | 107.57(13) |
| Mg(1)-O(1)#4 | 2.0430(18) | O(1)-P(1)-O(7) | 104.23(8) |
| Mg(1)-O(5)#5 | 2.0947(16) | O(1)#8-P(1)-O(7) | 104.22(8) |
| Mg(1)-O(2)#6 | 2.0986(17) | O(2)#8-P(2)-O(2) | 112.57(13) |
| Mg(1)-O(3)#7 | 2.1042(16) | O(2)#8-P(2)-O(5) | 114.28(7) |
| Mg(1)-O(1) | 2.1658(17) | O(2)-P(2)-O(5) | 114.28(7) |
| P(1)-O(3) | 1.514(2) | O(2)#8-P(2)-O(6) | 106.86(8) |
| P(1)-O(1) | 1.5174(16) | O(2)-P(2)-O(6) | 106.86(8) |
| P(1)-O(1)#8 | 1.5174(16) | O(5)-P(2)-O(6) | 100.69(12) |
| P(1)-O(7) | 1.601(2) | O(4)-P(3)-O(4)#8 | 116.16(13) |
| P(2)-O(2)#8 | 1.5118(16) | O(4)-P(3)-O(7) | 111.47(8) |
| P(2)-O(2) | 1.5118(16) | O(4)#8-P(3)-O(7) | 111.47(8) |
| P(2)-O(5) | 1.518(2) | O(4)-P(3)-O(6) | 108.95(8) |
| P(2)-O(6) | 1.632(2) | O(4)#8-P(3)-O(6) | 108.95(8) |
| P(3)-O(4) | 1.4921(16) | O(7)-P(3)-O(6) | 98.29(12) |
| P(3)-O(4)#8 | 1.4921(16) | O(4)#2-Mg(1)-O(1)#4 | 93.25(8) |
| P(3)-O(7) | 1.562(2) | O(4)#2-Mg(1)-O(5)#5 | 93.60(7) |
| P(3)-O(6) | 1.594(2) | O(1)#4-Mg(1)-O(5)#5 | 160.36(8) |
| O(1)-Mg(1)#4 | 2.0431(18) | O(4)#2-Mg(1)-O(2)#6 | 81.73(7) |
| O(2)-Mg(1)#3 | 2.0986(17) | O(1)#4-Mg(1)-O(2)#6 | 111.90(7) |
| O(3)-Mg(1)#10 | 2.1042(16) | O(5)#5-Mg(1)-O(2)#6 | 87.30(8) |
| O(3)-Mg(1)#11 | 2.1042(16) | O(4)#2-Mg(1)-O(3)#7 | 166.54(8) |
| O(4)-Mg(1)#2 | 2.0260(18) | O(1)#4-Mg(1)-O(3)#7 | 92.37(7) |
| O(5)-Mg(1)#12 | 2.0947(16) | O(5)#5-Mg(1)-O(3)#7 | 85.08(7) |
| O(5)-Mg(1)#13 | 2.0947(16) | O(2)#6-Mg(1)-O(3)#7 | 84.83(8) |
| O(2)-Li(1)-O(2)#1 | 180 | O(4)#2-Mg(1)-O(1) | 108.37(7) |
| O(2)-Li(1)-O(4)#1 | 82.41(6) | O(1)#4-Mg(1)-O(1) | 79.58(7) |
| O(2)#1-Li(1)-O(4)#1 | 97.59(6) | O(5)#5-Mg(1)-O(1) | 80.80(8) |
| O(2)-Li(1)-O(4) | 97.59(6) | O(2)#6-Mg(1)-O(1) | 164.75(8) |
| O(2)#1-Li(1)-O(4) | 82.41(6) | O(3)#7-Mg(1)-O(1) | 84.68(8) |

**Table S2a.** Selected bond distances (Å) and angles (deg.) for $LiMg_2P_3O_{10}$.

Symmetry transformations used to generate equivalent atoms:

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

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

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

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

**Table S2b.** Selected bond distances (Å) and angles (deg.) for $CsMg_2P_3O_{10}$.

| | | | |
|---|---|---|---|
| Cs(1)-O(2)#1 | 3.2701(19) | O(2)#1-Cs(1)-O(3)#2 | 44.24(5) |
| Cs(1)-O(2) | 3.2701(19) | O(2)-Cs(1)-O(3)#2 | 146.91(5) |
| Cs(1)-O(3)#2 | 3.312(2) | O(2)#1-Cs(1)-O(3)#3 | 146.91(5) |
| Cs(1)-O(3)#3 | 3.312(2) | O(2)-Cs(1)-O(3)#3 | 44.24(5) |
| Cs(1)-O(3)#4 | 3.403(2) | O(3)#2-Cs(1)-O(3)#3 | 137.74(7) |
| Cs(1)-O(3)#5 | 3.403(2) | O(2)#1-Cs(1)-O(3)#4 | 69.22(5) |
| Cs(1)-O(4)#6 | 3.523(2) | O(2)-Cs(1)-O(3)#4 | 92.43(5) |
| Cs(1)-O(4)#7 | 3.523(2) | O(3)#2-Cs(1)-O(3)#4 | 91.04(3) |
| Mg(1)-O(5)#6 | 1.938(2) | O(3)#3-Cs(1)-O(3)#4 | 130.57(6) |
| Mg(1)-O(4)#10 | 1.985(2) | O(2)#1-Cs(1)-O(3)#5 | 92.43(5) |
| Mg(1)-O(1) | 1.986(2) | O(2)-Cs(1)-O(3)#5 | 69.22(5) |
| Mg(1)-O(3)#11 | 2.009(2) | O(3)#2-Cs(1)-O(3)#5 | 130.57(6) |
| Mg(1)-O(1)#11 | 2.177(2) | O(3)#3-Cs(1)-O(3)#5 | 91.04(3) |
| P(1)-O(3) | 1.492(2) | O(3)#4-Cs(1)-O(3)#5 | 43.97(7) |
| P(1)-O(3)#3 | 1.492(2) | O(2)#1-Cs(1)-O(4)#6 | 90.90(5) |
| P(1)-O(2) | 1.588(2) | O(2)-Cs(1)-O(4)#6 | 103.71(5) |
| P(1)-O(2)#3 | 1.588(2) | O(3)#2-Cs(1)-O(4)#6 | 46.86(5) |
| P(2)-O(5) | 1.491(2) | O(3)#3-Cs(1)-O(4)#6 | 98.22(5) |
| P(2)-O(4) | 1.497(2) | O(3)#4-Cs(1)-O(4)#6 | 117.86(5) |
| P(2)-O(1) | 1.527(2) | O(3)#5-Cs(1)-O(4)#6 | 157.49(5) |
| P(2)-O(2) | 1.6448(19) | O(2)#1-Cs(1)-O(4)#7 | 103.71(5) |
| O(1)-Mg(1)#11 | 2.177(2) | O(2)-Cs(1)-O(4)#7 | 90.90(5) |
| O(3)-Mg(1)#11 | 2.009(2) | O(3)#2-Cs(1)-O(4)#7 | 98.22(5) |
| O(4)-Mg(1)#16 | 1.985(2) | O(3)#3-Cs(1)-O(4)#7 | 46.86(5) |
| O(5)-Mg(1)#4 | 1.938(2) | O(3)#4-Cs(1)-O(4)#7 | 157.49(5) |
| O(3)-Cs(1)#14 | 3.312(2) | O(3)#5-Cs(1)-O(4)#7 | 117.86(5) |
| O(3)-Cs(1)#13 | 3.403(2) | O(4)#6-Cs(1)-O(4)#7 | 82.79(7) |
| O(4)-Cs(1)#15 | 3.523(2) | O(3)-P(1)-O(3)#3 | 117.25(17) |
| O(5)#6-Mg(1)-O(4)#10 | 94.23(10) | O(3)-P(1)-O(2) | 109.87(10) |
| O(5)#6-Mg(1)-O(1) | 111.09(10) | O(3)#3-P(1)-O(2) | 107.14(11) |
| O(4)#10-Mg(1)-O(1) | 103.37(10) | O(3)-P(1)-O(2)#3 | 107.14(11) |
| O(5)#6-Mg(1)-O(3)#11 | 136.71(10) | O(3)#3-P(1)-O(2)#3 | 109.87(10) |
| O(4)#10-Mg(1)-O(3)#11 | 86.03(9) | O(2)-P(1)-O(2)#3 | 104.91(15) |
| O(1)-Mg(1)-O(3)#11 | 110.91(9) | O(5)-P(2)-O(4) | 116.65(13) |
| O(5)#6-Mg(1)-O(1)#11 | 90.09(9) | O(5)-P(2)-O(1) | 114.28(12) |
| O(4)#10-Mg(1)-O(1)#11 | 172.94(9) | O(4)-P(2)-O(1) | 111.39(12) |
| O(1)-Mg(1)-O(1)#11 | 80.19(9) | O(5)-P(2)-O(2) | 103.03(11) |
| O(3)#11-Mg(1)-O(1)#11 | 87.00(8) | O(4)-P(2)-O(2) | 105.45(11) |
| O(2)#1-Cs(1)-O(2) | 160.61(7) | O(1)-P(2)-O(2) | 104.44(11) |

Symmetry transformations used to generate equivalent atoms:

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

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

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

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

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

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

#15 x-1/2,y+1/2,-z+1/2 #16 x-1/2,-y+1/2,-z

**Table S2c.** Selected bond distances (Å) and angles (deg.) for $Rb_2MgP_2O_7$.

| | | | |
|---|---|---|---|
| P(1)-O(1) | 1.473(12) | O(2)#13-Rb(1)-O(2) | 100.33(19) |
| P(1)-O(5)#1 | 1.509(7) | O(5)#14-Rb(1)-O(2) | 126.1(2) |
| P(1)-O(5) | 1.509(7) | O(5)#11-Rb(1)-O(2) | 103.8(2) |
| P(1)-O(4) | 1.621(12) | O(2)#6-Rb(1)-O(2)#1 | 100.33(19) |
| P(2)-O(3) | 1.488(14) | O(2)#13-Rb(1)-O(2)#1 | 79.1(3) |
| P(2)-O(2)#1 | 1.488(8) | O(5)#14-Rb(1)-O(2)#1 | 103.8(2) |
| P(2)-O(2) | 1.488(8) | O(5)#11-Rb(1)-O(2)#1 | 126.1(2) |
| P(2)-O(4) | 1.648(12) | O(2)-Rb(1)-O(2)#1 | 46.9(3) |
| Mg(1)-O(1) | 1.984(13) | O(2)#6-Rb(1)-O(1)#2 | 148.4(2) |
| Mg(1)-O(2)#8 | 2.038(9) | O(2)#13-Rb(1)-O(1)#2 | 95.1(3) |
| Mg(1)-O(2)#4 | 2.038(9) | O(5)#14-Rb(1)-O(1)#2 | 46.6(3) |
| Mg(1)-O(5)#4 | 2.055(8) | O(5)#11-Rb(1)-O(1)#2 | 92.3(3) |
| Mg(1)-O(5)#8 | 2.055(8) | O(2)-Rb(1)-O(1)#2 | 98.3(3) |
| O(1)-Rb(1)#3 | 3.182(8) | O(2)#1-Rb(1)-O(1)#2 | 59.4(2) |
| O(1)-Rb(1)#4 | 3.182(8) | O(2)#6-Rb(1)-O(1)#11 | 95.1(3) |
| O(2)-Mg(1)#11 | 2.038(9) | O(2)#13-Rb(1)-O(1)#11 | 148.4(2) |
| O(2)-Rb(1)#6 | 2.984(10) | O(5)#14-Rb(1)-O(1)#11 | 92.3(3) |
| O(2)-Rb(1) | 3.106(10) | O(5)#11-Rb(1)-O(1)#11 | 46.6(3) |
| O(2)-Rb(2)#5 | 3.548(11) | O(2)-Rb(1)-O(1)#11 | 59.4(2) |
| O(3)-Rb(2)#12 | 2.662(15) | O(2)#1-Rb(1)-O(1)#11 | 98.3(3) |
| O(3)-Rb(1)#6 | 3.347(10) | O(1)#2-Rb(1)-O(1)#11 | 110.7(4) |
| O(3)-Rb(1)#7 | 3.347(10) | O(2)#6-Rb(1)-O(3)#6 | 46.3(3) |
| O(3)-Rb(2) | 3.582(11) | O(2)#13-Rb(1)-O(3)#6 | 92.0(3) |
| O(3)-Rb(2)#5 | 3.582(11) | O(5)#14-Rb(1)-O(3)#6 | 114.2(3) |
| O(4)-Rb(2)#5 | 2.997(7) | O(5)#11-Rb(1)-O(3)#6 | 73.7(3) |
| O(4)-Rb(2) | 2.997(7) | O(2)-Rb(1)-O(3)#6 | 98.4(3) |
| O(5)-Mg(1)#11 | 2.055(8) | O(2)#1-Rb(1)-O(3)#6 | 140.2(3) |
| O(5)-Rb(2)#2 | 3.003(8) | O(1)#2-Rb(1)-O(3)#6 | 160.3(3) |
| O(5)-Rb(1)#4 | 3.075(8) | O(1)#11-Rb(1)-O(3)#6 | 69.8(3) |
| Rb(1)-O(2)#6 | 2.984(10) | O(2)#6-Rb(1)-O(3)#7 | 92.0(3) |
| Rb(1)-O(2)#13 | 2.984(10) | O(2)#13-Rb(1)-O(3)#7 | 46.3(3) |
| Rb(1)-O(5)#14 | 3.075(9) | O(5)#14-Rb(1)-O(3)#7 | 73.7(3) |
| Rb(1)-O(5)#11 | 3.075(8) | O(5)#11-Rb(1)-O(3)#7 | 114.2(3) |
| Rb(1)-O(2)#1 | 3.106(10) | O(2)-Rb(1)-O(3)#7 | 140.2(3) |
| Rb(1)-O(1)#2 | 3.182(8) | O(2)#1-Rb(1)-O(3)#7 | 98.4(3) |
| Rb(1)-O(1)#11 | 3.182(8) | O(1)#2-Rb(1)-O(3)#7 | 69.8(3) |
| Rb(1)-O(3)#6 | 3.347(10) | O(1)#11-Rb(1)-O(3)#7 | 160.3(3) |
| Rb(1)-O(3)#7 | 3.347(10) | O(3)#6-Rb(1)-O(3)#7 | 102.9(4) |
| Rb(2)-O(3)#12 | 2.662(15) | O(3)#12-Rb(2)-O(4)#15 | 116.4(2) |
| Rb(2)-O(4)#15 | 2.997(7) | O(3)#12-Rb(2)-O(4) | 116.4(2) |
| Rb(2)-O(5)#8 | 3.003(8) | O(4)#15-Rb(2)-O(4) | 121.8(4) |

| | | | |
|---|---|---|---|
| Rb(2)-O(5)#3 | 3.003(8) | O(3)#12-Rb(2)-O(5)#8 | 85.6(4) |
| Rb(2)-O(2)#15 | 3.548(11) | O(4)#15-Rb(2)-O(5)#8 | 125.3(3) |
| Rb(2)-O(2)#1 | 3.548(11) | O(4)-Rb(2)-O(5)#8 | 81.1(3) |
| Rb(2)-O(3)#15 | 3.582(11) | O(3)#12-Rb(2)-O(5)#3 | 85.6(4) |
| O(1)-P(1)-O(5)#1 | 112.4(4) | O(4)#15-Rb(2)-O(5)#3 | 81.1(3) |
| O(1)-P(1)-O(5) | 112.4(4) | O(4)-Rb(2)-O(5)#3 | 125.3(3) |
| O(5)#1-P(1)-O(5) | 113.1(6) | O(5)#8-Rb(2)-O(5)#3 | 49.6(3) |
| O(1)-P(1)-O(4) | 105.1(7) | O(3)#12-Rb(2)-O(2)#15 | 121.8(3) |
| O(5)#1-P(1)-O(4) | 106.6(4) | O(4)#15-Rb(2)-O(2)#15 | 43.6(2) |
| O(5)-P(1)-O(4) | 106.6(4) | O(4)-Rb(2)-O(2)#15 | 87.6(3) |
| O(3)-P(2)-O(2)#1 | 115.1(5) | O(5)#8-Rb(2)-O(2)#15 | 152.5(2) |
| O(3)-P(2)-O(2) | 115.1(5) | O(5)#3-Rb(2)-O(2)#15 | 124.1(2) |
| O(2)#1-P(2)-O(2) | 112.2(8) | O(3)#12-Rb(2)-O(2)#1 | 121.8(3) |
| O(3)-P(2)-O(4) | 103.2(7) | O(4)#15-Rb(2)-O(2)#1 | 87.6(3) |
| O(2)#1-P(2)-O(4) | 104.8(5) | O(4)-Rb(2)-O(2)#1 | 43.6(2) |
| O(2)-P(2)-O(4) | 104.8(5) | O(5)#8-Rb(2)-O(2)#1 | 124.1(2) |
| O(1)-Mg(1)-O(2)#8 | 101.4(4) | O(5)#3-Rb(2)-O(2)#1 | 152.5(2) |
| O(1)-Mg(1)-O(2)#4 | 101.4(4) | O(2)#15-Rb(2)-O(2)#1 | 45.9(2) |
| O(2)#8-Mg(1)-O(2)#4 | 85.5(5) | O(3)#12-Rb(2)-O(3) | 85.1(3) |
| O(1)-Mg(1)-O(5)#4 | 108.8(4) | O(4)#15-Rb(2)-O(3) | 122.9(3) |
| O(2)#8-Mg(1)-O(5)#4 | 149.8(5) | O(4)-Rb(2)-O(3) | 42.8(3) |
| O(2)#4-Mg(1)-O(5)#4 | 88.1(3) | O(5)#8-Rb(2)-O(3) | 107.4(2) |
| O(1)-Mg(1)-O(5)#8 | 108.8(4) | O(5)#3-Rb(2)-O(3) | 155.9(2) |
| O(2)#8-Mg(1)-O(5)#8 | 88.1(3) | O(2)#15-Rb(2)-O(3) | 79.5(3) |
| O(2)#4-Mg(1)-O(5)#8 | 149.8(5) | O(2)#1-Rb(2)-O(3) | 41.3(3) |
| O(5)#4-Mg(1)-O(5)#8 | 82.8(5) | O(3)#12-Rb(2)-O(3)#15 | 85.1(3) |
| O(2)#6-Rb(1)-O(2)#13 | 55.2(3) | O(4)#15-Rb(2)-O(3)#15 | 42.8(3) |
| O(2)#6-Rb(1)-O(5)#14 | 153.4(3) | O(4)-Rb(2)-O(3)#15 | 122.9(3) |
| O(2)#13-Rb(1)-O(5)#14 | 119.0(2) | O(5)#8-Rb(2)-O(3)#15 | 155.9(2) |
| O(2)#6-Rb(1)-O(5)#11 | 119.0(2) | O(5)#3-Rb(2)-O(3)#15 | 107.4(2) |
| O(2)#13-Rb(1)-O(5)#11 | 153.4(3) | O(2)#15-Rb(2)-O(3)#15 | 41.3(3) |
| O(5)#14-Rb(1)-O(5)#11 | 52.5(3) | O(2)#1-Rb(2)-O(3)#15 | 79.5(3) |
| O(2)#6-Rb(1)-O(2) | 79.1(3) | O(3)-Rb(2)-O(3)#15 | 93.9(4) |

Symmetry transformations used to generate equivalent atoms:

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

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

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

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

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

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

#15 x,y+1,z

**Table S3.** EDS results for $LiMg_2P_3O_{10}$ (a), $CsMg_2P_3O_{10}$ (b) and $Rb_2MgP_2O_7$ (c).

(a)

| Point 1 | | | | Point 2 | | | |
|---|---|---|---|---|---|---|---|
| Element | Weight % | Atomic % | Formula | Element | Weight % | Atomic % | Formula |
| Mg | 15.75 | 17.98 | 2.0 | Mg | 15.85 | 17.79 | 2.0 |
| P | 30.12 | 32.28 | 3.2 | P | 31.23 | 33.32 | 3.1 |
| O | 54.13 | 49.74 | □ | O | 52.92 | 48.89 | □ |
| Toals | 100 | □ | □ | Toals | 100 | □ | □ |
| Point 3 | | | | □ | | | |
| Element | Weight % | Atomic % | Formula | □ | | | |
| Mg | 16.83 | 18.23 | 2.1 | □ | Average ratio | | □ |
| P | 29.82 | 32.35 | 3.0 | □ | | | □ |
| O | 53.35 | 49.42 | □ | □ | $Mg_{2.0}P_{3.1}$ | | □ |
| Toals | 100 | □ | □ | □ | | | □ |

(b)

| Point 1 | | | | Point 2 | | | |
|---|---|---|---|---|---|---|---|
| Element | Weight % | Atomic % | Formula | Element | Weight % | Atomic % | Formula |
| Cs | 31.59 | 9.89 | 1.1 | Cs | 32.31 | 9.93 | 1.2 |
| Mg | 12.13 | 18.37 | 2.0 | Mg | 13.15 | 19.02 | 2.0 |
| P | 20.83 | 31.56 | 3.1 | P | 21.02 | 30.79 | 3.0 |
| O | 35.45 | 40.81 | □ | O | 33.52 | 40.26 | □ |
| Toals | 100 | □ | □ | Toals | 100 | □ | □ |
| Point 3 | | | | □ | | | |
| Element | Weight % | Atomic % | Formula | □ | | | |
| Cs | 30.87 | 9.35 | 1.0 | □ | Average ratio | | □ |
| Mg | 12.34 | 19.15 | 2.1 | □ | | | □ |
| P | 21.83 | 29.89 | 3.2 | □ | | | □ |
| O | 34.96 | 41.61 | □ | □ | $Cs_{1.1}Mg_{2.0}P_{3.1}$ | | □ |
| Toals | 100 | □ | □ | □ | □ | □ | □ |

(c)

| Point 1 | | | | Point 2 | | | |
|---|---|---|---|---|---|---|---|
| Element | Weight % | Atomic % | Formula | Element | Weight % | Atomic % | Formula |
| Rb | 48.73 | 18.78 | 2.1 | Cs | 47.76 | 19.39 | 2.2 |
| Mg | 6.23 | 13.23 | 1.2 | Mg | 7.45 | 10.32 | 1.0 |
| P | 15.98 | 19.54 | 2.2 | P | 17.48 | 18.43 | 2.2 |
| O | 29.06 | 48.45 | □ | O | 27.31 | 51.86 | □ |
| Toals | 100 | □ | □ | Toals | 100 | □ | □ |
| Point 3 | | | | □ | | | |
| Element | Weight % | Atomic % | Formula | □ | | | |
| Cs | 45.36 | 20.32 | 2.0 | □ | Average ratio | | □ |
| Mg | 5.98 | 9.97 | 1.1 | □ | | | □ |
| P | 15.87 | 17.63 | 2.1 | □ | $Rb_{2.1}Mg_{1.1}P_{2.1}$ | | □ |
| O | 32.79 | 52.08 | □ | □ | | | □ |
| Toals | 100 | □ | □ | □ | □ | □ | □ |

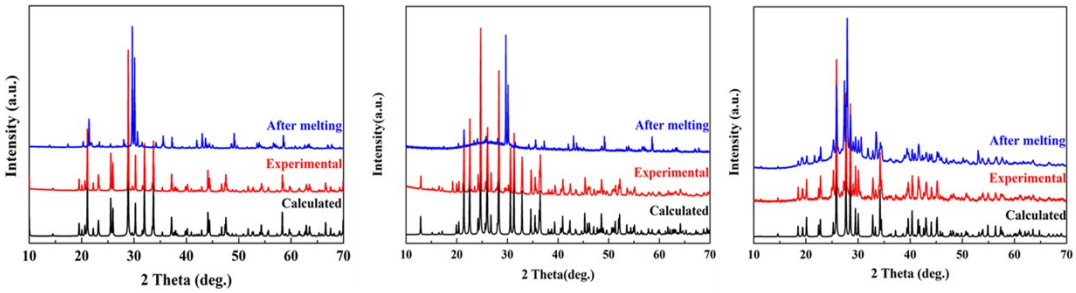


**Figure S1.** Experimental and calculated XRD patterns for (a) $LiMg_2P_3O_{10}$, (b) $CsMg_2P_3O_{10}$ and (c) $Rb_2MgP_2O_7$.

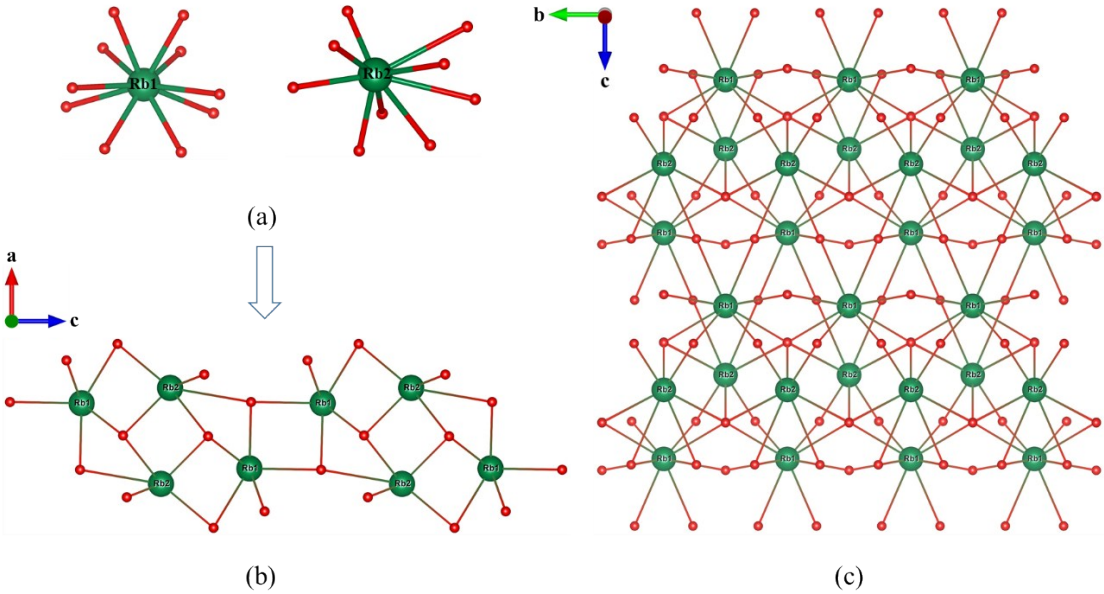


**Figure S2**. (a) The ten-coordinated Rb(1) and nine-coordinated Rb(2) cations; (b) the 2D Rb-O layers extending in *ac* plane; (c) the 2D Rb-O layers extending in *bc* plane.

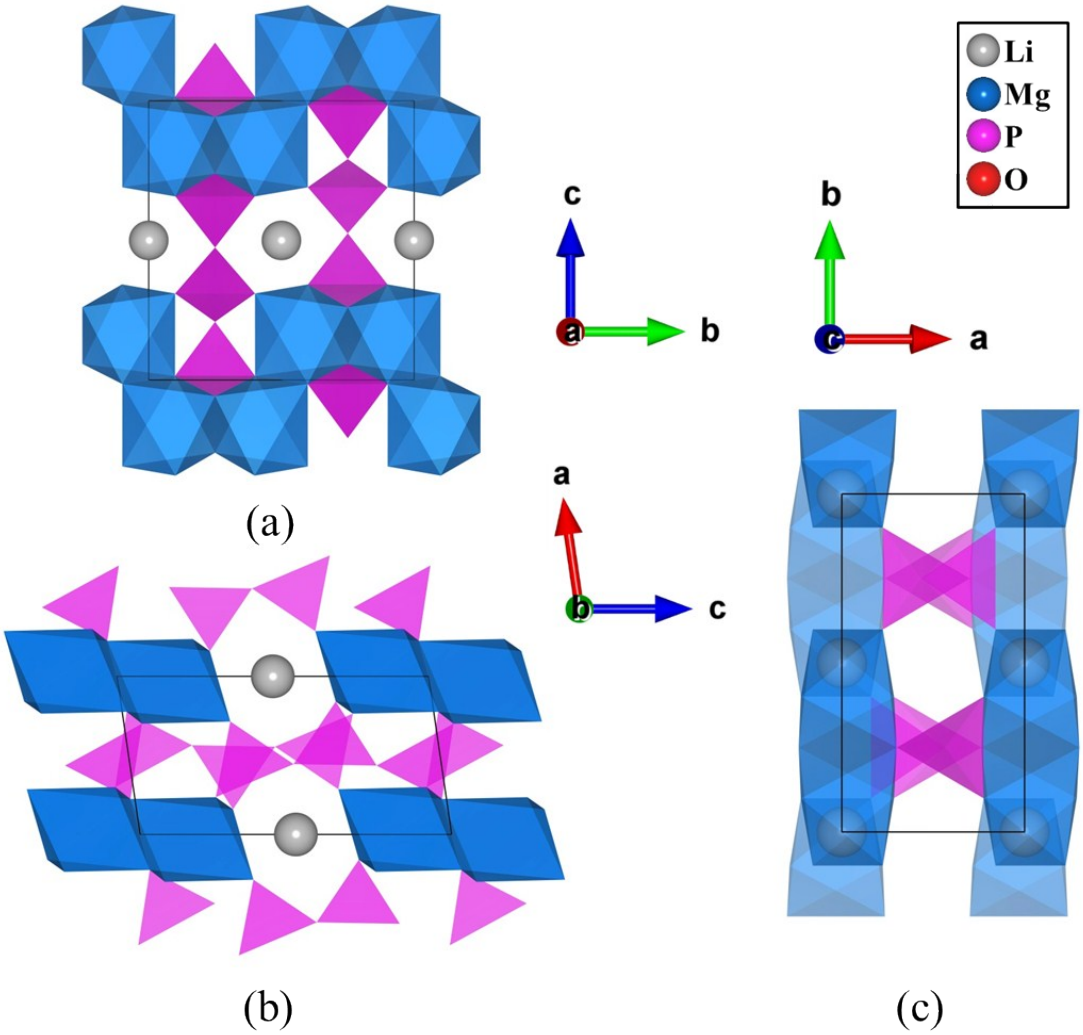


**Figure S3**. Structure of $LiMg_3P_3O_{10}$ viewed along the (a) *a*-axis, (b) *b*-axis and (c) *c*-axis directions.