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# $AMgPO_4 \cdot 6H_2O$ (A=Rb, Cs): strong SHG responses originated from orderly $PO_4$ groups

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Table S1. Atomic coordinates (Å×$10^4$) and equivalent isotropic displacements parameters (Å$^2$×$10^3$) for $RbMgPO_4 \cdot 6H_2O$

| atoms | x | y | z | U(eq) | BVS |
|---|---|---|---|---|---|
| Rb(1) | 5000 | 6498(1) | 3988(1) | 49(1) | 0.85 |
| Mg(1) | 0 | 3869(4) | 2528(2) | 24(1) | 2.00 |
| P(1) | 5000 | 10167(3) | 1201(2) | 23(1) | 4.70 |
| O(1) | 5000 | 10404(7) | 2553(4) | 27(1) | 1.78 |
| O(2) | 3172(4) | 8959(5) | 791(3) | 25(1) | 1.81 |
| O(3) | 5000 | 12450(7) | 634(4) | 30(1) | 1.81 |
| O(4) | 2131(5) | 4980(7) | 1400(4) | 38(1) | 1.88 |
| O(5) | 0 | 891(8) | 1609(5) | 39(2) | 2.01 |
| O(6) | 2213(5) | 2709(5) | 3623(3) | 32(1) | 1.86 |
| O(7) | 0 | 6976(8) | 3343(4) | 42(2) | 1.94 |

Table S2. Hydrogen coordinates (Å×$10^4$) and isotropic displacement parameters (Å$^2$×$10^3$) for $RbMgPO_4 \cdot 6H_2O$

| atoms | x | y | z | U(eq) |
|---|---|---|---|---|
| H(4A) | 2310(60) | 6280(20) | 1320(50) | 57 |
| H(4B) | 3000(50) | 4180(50) | 1180(50) | 57 |
| H(6A) | 3030(50) | 1980(70) | 3250(30) | 48 |
| H(6B) | 1960(70) | 2150(70) | 4270(20) | 48 |
| H(7A) | 0 | 8120(20) | 2958(17) | 64 |
| H(7B) | 0 | 7200(30) | 4065(10) | 64 |
| H(5) | 1007 | 23 | 1245 | 64 |

Table S3. Bond lengths (Å) for $RbMgPO_4 \cdot 6H_2O$

| | | | |
|---|---|---|---|
| Rb(1)-O(1) | 2.915(5) | O(4)#2-Rb(1)-Mg(1)#4 | 81.34(9) |
| Rb(1)-O(6) | 3.061(4) | O(4)#3-Rb(1)-Mg(1)#4 | 127.05(8) |
| Rb(1)-O(6)#1 | 3.061(4) | O(5)#3-Rb(1)-Mg(1)#4 | 122.49(4) |
| Rb(1)-O(4)#2 | 3.237(5) | O(7)-Rb(1)-Mg(1)#4 | 139.36(9) |
| Rb(1)-O(4)#3 | 3.237(5) | O(7)#4-Rb(1)-Mg(1)#4 | 30.89(9) |
| Rb(1)-O(5)#3 | 3.383(6) | P(1)-Rb(1)-Mg(1)#4 | 84.55(5) |
| Rb(1)-O(7) | 3.537(3) | Mg(1)#3-Rb(1)-Mg(1)#4 | 112.06(4) |
| Rb(1)-O(7)#4 | 3.537(3) | Mg(1)-Rb(1)-Mg(1)#4 | 112.08(8) |
| Rb(1)-P(1) | 3.892(3) | O(1)-Rb(1)-H(6A) | 125.1(8) |
| Rb(1)-Mg(1)#3 | 4.021(4) | O(6)-Rb(1)-H(6A) | 15.0(3) |
| Rb(1)-Mg(1) | 4.157(3) | O(6)#1-Rb(1)-H(6A) | 64.2(5) |
| Rb(1)-Mg(1)#4 | 4.157(3) | O(4)#2-Rb(1)-H(6A) | 99.5(8) |
| Rb(1)-H(6A) | 3.22(5) | O(4)#3-Rb(1)-H(6A) | 77.4(6) |
| Mg(1)-O(4)#5 | 2.066(4) | O(5)#3-Rb(1)-H(6A) | 130.0(6) |
| Mg(1)-O(4) | 2.066(4) | O(7)-Rb(1)-H(6A) | 66.9(6) |
| Mg(1)-O(6) | 2.094(4) | O(7)#4-Rb(1)-H(6A) | 115.5(3) |
| Mg(1)-O(6)#5 | 2.094(4) | P(1)-Rb(1)-H(6A) | 107.2(8) |

| | | | |
|---|---|---|---|
| Mg(1)-O(5) | 2.118(5) | Mg(1)#3-Rb(1)-H(6A) | 102.1(7) |
| Mg(1)-O(7) | 2.134(6) | Mg(1)-Rb(1)-H(6A) | 37.5(7) |
| Mg(1)-Rb(1)#6 | 4.021(4) | Mg(1)#4-Rb(1)-H(6A) | 84.6(3) |
| Mg(1)-Rb(1)#7 | 4.157(3) | O(4)#5-Mg(1)-O(4) | 90.7(3) |
| P(1)-O(2) | 1.538(3) | O(4)#5-Mg(1)-O(6) | 178.13(19) |
| P(1)-O(2)#1 | 1.538(3) | O(4)-Mg(1)-O(6) | 87.88(16) |
| P(1)-O(1) | 1.540(5) | O(4)#5-Mg(1)-O(6)#5 | 87.88(16) |
| P(1)-O(3) | 1.553(4) | O(4)-Mg(1)-O(6)#5 | 178.13(19) |
| O(4)-Rb(1)#6 | 3.237(5) | O(6)-Mg(1)-O(6)#5 | 93.5(2) |
| O(4)-H(4A) | 0.819(10) | O(4)#5-Mg(1)-O(5) | 89.15(18) |
| O(4)-H(4B) | 0.813(10) | O(4)-Mg(1)-O(5) | 89.15(18) |
| O(5)-Rb(1)#6 | 3.383(6) | O(6)-Mg(1)-O(5) | 89.63(15) |
| O(5)-H(5) | 0.97 | O(6)#5-Mg(1)-O(5) | 89.63(15) |
| O(6)-H(6A) | 0.834(10) | O(4)#5-Mg(1)-O(7) | 88.16(16) |
| O(6)-H(6B) | 0.831(10) | O(4)-Mg(1)-O(7) | 88.16(16) |
| O(7)-Rb(1)#7 | 3.537(3) | O(6)-Mg(1)-O(7) | 92.99(15) |
| O(7)-H(7A) | 0.830(10) | O(6)#5-Mg(1)-O(7) | 92.99(15) |
| O(7)-H(7B) | 0.831(10) | O(5)-Mg(1)-O(7) | 176.2(2) |
| O(1)-Rb(1)-O(6) | 124.07(9) | O(4)#5-Mg(1)-Rb(1)#6 | 53.19(14) |
| O(1)-Rb(1)-O(6)#1 | 124.07(9) | O(4)-Mg(1)-Rb(1)#6 | 53.19(14) |
| O(6)-Rb(1)-O(6)#1 | 77.80(14) | O(6)-Mg(1)-Rb(1)#6 | 124.94(11) |
| O(1)-Rb(1)-O(4)#2 | 134.94(10) | O(6)#5-Mg(1)-Rb(1)#6 | 124.94(11) |
| O(6)-Rb(1)-O(4)#2 | 100.53(10) | O(5)-Mg(1)-Rb(1)#6 | 57.27(16) |
| O(6)#1-Rb(1)-O(4)#2 | 67.21(10) | O(7)-Mg(1)-Rb(1)#6 | 118.90(14) |
| O(1)-Rb(1)-O(4)#3 | 134.94(10) | O(4)#5-Mg(1)-Rb(1) | 134.92(15) |
| O(6)-Rb(1)-O(4)#3 | 67.21(10) | O(4)-Mg(1)-Rb(1) | 61.72(14) |
| O(6)#1-Rb(1)-O(4)#3 | 100.53(10) | O(6)-Mg(1)-Rb(1) | 45.07(11) |
| O(4)#2-Rb(1)-O(4)#3 | 54.00(14) | O(6)#5-Mg(1)-Rb(1) | 120.15(13) |
| O(1)-Rb(1)-O(5)#3 | 95.40(13) | O(5)-Mg(1)-Rb(1) | 122.48(5) |
| O(6)-Rb(1)-O(5)#3 | 119.02(9) | O(7)-Mg(1)-Rb(1) | 58.30(5) |
| O(6)#1-Rb(1)-O(5)#3 | 119.02(9) | Rb(1)#6-Mg(1)-Rb(1) | 114.83(4) |
| O(4)#2-Rb(1)-O(5)#3 | 52.61(11) | O(4)#5-Mg(1)-Rb(1)#7 | 61.72(14) |
| O(4)#3-Rb(1)-O(5)#3 | 52.61(11) | O(4)-Mg(1)-Rb(1)#7 | 134.92(15) |
| O(1)-Rb(1)-O(7) | 79.34(7) | O(6)-Mg(1)-Rb(1)#7 | 120.15(13) |
| O(6)-Rb(1)-O(7) | 54.83(10) | O(6)#5-Mg(1)-Rb(1)#7 | 45.07(11) |
| O(6)#1-Rb(1)-O(7) | 130.41(11) | O(5)-Mg(1)-Rb(1)#7 | 122.48(5) |
| O(4)#2-Rb(1)-O(7) | 129.87(10) | O(7)-Mg(1)-Rb(1)#7 | 58.30(5) |
| O(4)#3-Rb(1)-O(7) | 75.88(10) | Rb(1)#6-Mg(1)-Rb(1)#7 | 114.83(4) |
| O(5)#3-Rb(1)-O(7) | 98.15(8) | Rb(1)-Mg(1)-Rb(1)#7 | 112.07(8) |
| O(1)-Rb(1)-O(7)#4 | 79.34(7) | O(2)-P(1)-O(2)#1 | 110.1(3) |
| O(6)-Rb(1)-O(7)#4 | 130.41(11) | O(2)-P(1)-O(1) | 110.32(18) |
| O(6)#1-Rb(1)-O(7)#4 | 54.83(10) | O(2)#1-P(1)-O(1) | 110.32(18) |
| O(4)#2-Rb(1)-O(7)#4 | 75.88(10) | O(2)-P(1)-O(3) | 108.51(17) |
| O(4)#3-Rb(1)-O(7)#4 | 129.87(10) | O(2)#1-P(1)-O(3) | 108.51(17) |

| | | | |
|---|---|---|---|
| O(5)#3-Rb(1)-O(7)#4 | 98.15(8) | O(1)-P(1)-O(3) | 109.0(3) |
| O(7)-Rb(1)-O(7)#4 | 154.21(14) | O(2)-P(1)-Rb(1) | 87.80(16) |
| O(1)-Rb(1)-P(1) | 20.35(8) | O(2)#1-P(1)-Rb(1) | 87.80(16) |
| O(6)-Rb(1)-P(1) | 109.72(7) | O(1)-P(1)-Rb(1) | 41.16(17) |
| O(6)#1-Rb(1)-P(1) | 109.72(7) | O(3)-P(1)-Rb(1) | 150.18(19) |
| O(4)#2-Rb(1)-P(1) | 148.34(8) | P(1)-O(1)-Rb(1) | 118.5(2) |
| O(4)#3-Rb(1)-P(1) | 148.34(8) | Mg(1)-O(4)-Rb(1)#6 | 96.09(16) |
| O(5)#3-Rb(1)-P(1) | 115.75(10) | Mg(1)-O(4)-H(4A) | 120(3) |
| O(7)-Rb(1)-P(1) | 77.48(7) | Rb(1)#6-O(4)-H(4A) | 104(4) |
| O(7)#4-Rb(1)-P(1) | 77.48(7) | Mg(1)-O(4)-H(4B) | 120(3) |
| O(1)-Rb(1)-Mg(1)#3 | 127.19(10) | Rb(1)#6-O(4)-H(4B) | 85(4) |
| O(6)-Rb(1)-Mg(1)#3 | 95.27(6) | H(4A)-O(4)-H(4B) | 117(2) |
| O(6)#1-Rb(1)-Mg(1)#3 | 95.27(6) | Mg(1)-O(5)-Rb(1)#6 | 90.94(18) |
| O(4)#2-Rb(1)-Mg(1)#3 | 30.73(7) | Mg(1)-O(5)-H(5) | 133.7 |
| O(4)#3-Rb(1)-Mg(1)#3 | 30.73(7) | Rb(1)#6-O(5)-H(5) | 83.8 |
| O(5)#3-Rb(1)-Mg(1)#3 | 31.78(9) | Mg(1)-O(6)-Rb(1) | 105.96(13) |
| O(7)-Rb(1)-Mg(1)#3 | 102.20(7) | Mg(1)-O(6)-H(6A) | 112(3) |
| O(7)#4-Rb(1)-Mg(1)#3 | 102.20(7) | Rb(1)-O(6)-H(6A) | 93(4) |
| P(1)-Rb(1)-Mg(1)#3 | 147.54(6) | Mg(1)-O(6)-H(6B) | 121(3) |
| O(1)-Rb(1)-Mg(1) | 95.88(7) | Rb(1)-O(6)-H(6B) | 109(4) |
| O(6)-Rb(1)-Mg(1) | 28.97(6) | H(6A)-O(6)-H(6B) | 111.5(18) |
| O(6)#1-Rb(1)-Mg(1) | 99.60(9) | Mg(1)-O(7)-Rb(1) | 90.81(9) |
| O(4)#2-Rb(1)-Mg(1) | 127.05(8) | Mg(1)-O(7)-Rb(1)#7 | 90.81(9) |
| O(4)#3-Rb(1)-Mg(1) | 81.34(9) | Rb(1)-O(7)-Rb(1)#7 | 154.21(14) |
| O(5)#3-Rb(1)-Mg(1) | 122.49(4) | Mg(1)-O(7)-H(7A) | 122.6(15) |
| O(7)-Rb(1)-Mg(1) | 30.89(9) | Rb(1)-O(7)-H(7A) | 100.4(2) |
| O(7)#4-Rb(1)-Mg(1) | 139.36(9) | Rb(1)#7-O(7)-H(7A) | 100.4(2) |
| P(1)-Rb(1)-Mg(1) | 84.55(5) | Mg(1)-O(7)-H(7B) | 125.2(14) |
| Mg(1)#3-Rb(1)-Mg(1) | 112.06(4) | Rb(1)-O(7)-H(7B) | 79.03(18) |
| O(1)-Rb(1)-Mg(1)#4 | 95.88(7) | Rb(1)#7-O(7)-H(7B) | 79.03(18) |
| O(6)-Rb(1)-Mg(1)#4 | 99.60(9) | H(7A)-O(7)-H(7B) | 112.2(18) |
| Rb(1)-O(1) | 2.915(5) | O(4)#2-Rb(1)-Mg(1)#4 | 81.34(9) |
| Rb(1)-O(6) | 3.061(4) | O(4)#3-Rb(1)-Mg(1)#4 | 127.05(8) |
| Rb(1)-O(6)#1 | 3.061(4) | O(5)#3-Rb(1)-Mg(1)#4 | 122.49(4) |

Symmetry transformations used to generate equivalent atoms:

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

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

#7 x-1,y,z

Table S4. Atomic coordinates (Å×$10^4$) and equivalent isotropic displacements parameters (Å$^2$×$10^3$) for $CsMgPO_4 \cdot 6H_2O$

| atoms | x | y | z | U(eq) | BVS |
|---|---|---|---|---|---|
| Cs(1) | 3333 | 6667 | 2643(1) | 44(1) | 0.72 |
| Mg(1) | 6667 | 3333 | 3886(2) | 19(1) | 2.13 |
| O(3) | 5231(2) | 462(4) | 4882(2) | 37(1) | 1.81 |
| O(4) | 8127(2) | 6253(4) | 2966(2) | 35(1) | 1.76 |
| P(1) | 0 | 0 | 5446(1) | 16(1) | 4.78 |
| O(1) | 1215(2) | 2429(3) | 5860(2) | 23(1) | 1.53 |
| O(2) | 0 | 0 | 4151(3) | 24(1) | 1.50 |

Table S5. Hydrogen coordinates (Å×$10^4$) and isotropic displacement parameters (Å$^2$×$10^3$) for $CsMgPO_4 \cdot 6H_2O$

| atoms | x | y | z | U(eq) |
|---|---|---|---|---|
| H(3) | 5950(60) | -100(70) | 5120(40) | 55 |
| H(4A) | 8714(19) | 7430(40) | 3340(30) | 53 |
| H(4B) | 8220(30) | 6440(60) | 2286(9) | 53 |

Table S6. Bond lengths (Å) for $CsMgPO_4 \cdot 6H_2O$

| | | | |
|---|---|---|---|
| Cs(1)-O(4)#1 | 3.4852(3) | O(3)#6-Cs(1)-O(3)#10 | 112.093(12) |
| Cs(1)-O(4)#2 | 3.4852(3) | O(3)#7-Cs(1)-O(3)#10 | 145.63(2) |
| Cs(1)-O(4)#3 | 3.4852(3) | O(3)#8-Cs(1)-O(3)#10 | 145.63(2) |
| Cs(1)-O(4)#4 | 3.4852(3) | O(3)#9-Cs(1)-O(3)#10 | 47.23(6) |
| Cs(1)-O(4) | 3.4852(3) | O(4)#1-Cs(1)-O(3)#11 | 118.61(4) |
| Cs(1)-O(4)#5 | 3.4852(3) | O(4)#2-Cs(1)-O(3)#11 | 97.53(3) |
| Cs(1)-O(3)#6 | 3.507(3) | O(4)#3-Cs(1)-O(3)#11 | 118.61(4) |
| Cs(1)-O(3)#7 | 3.507(3) | O(4)#4-Cs(1)-O(3)#11 | 97.53(3) |
| Cs(1)-O(3)#8 | 3.507(3) | O(4)-Cs(1)-O(3)#11 | 71.62(5) |
| Cs(1)-O(3)#9 | 3.716(3) | O(4)#5-Cs(1)-O(3)#11 | 71.62(5) |
| Cs(1)-O(3)#10 | 3.716(3) | O(3)#6-Cs(1)-O(3)#11 | 145.63(2) |
| Cs(1)-O(3)#11 | 3.716(3) | O(3)#7-Cs(1)-O(3)#11 | 145.63(2) |
| Mg(1)-O(4)#8 | 2.063(2) | O(3)#8-Cs(1)-O(3)#11 | 112.093(12) |
| Mg(1)-O(4)#5 | 2.063(2) | O(3)#9-Cs(1)-O(3)#11 | 47.23(6) |
| Mg(1)-O(4) | 2.063(2) | O(3)#10-Cs(1)-O(3)#11 | 47.23(6) |
| Mg(1)-O(3)#5 | 2.090(3) | O(4)#8-Mg(1)-O(4)#5 | 94.35(11) |
| Mg(1)-O(3) | 2.090(3) | O(4)#8-Mg(1)-O(4) | 94.35(11) |
| Mg(1)-O(3)#8 | 2.090(3) | O(4)#5-Mg(1)-O(4) | 94.35(11) |
| Mg(1)-Cs(1)#12 | 4.2561(7) | O(4)#8-Mg(1)-O(3)#5 | 87.39(7) |
| Mg(1)-Cs(1)#13 | 4.2561(7) | O(4)#5-Mg(1)-O(3)#5 | 177.43(14) |
| Mg(1)-Cs(1)#14 | 4.484(2) | O(4)-Mg(1)-O(3)#5 | 87.39(7) |
| O(3)-Cs(1)#12 | 3.507(3) | O(4)#8-Mg(1)-O(3) | 87.39(7) |
| O(3)-Cs(1)#14 | 3.716(3) | O(4)#5-Mg(1)-O(3) | 87.39(7) |
| O(3)-H(3) | 0.817(10) | O(4)-Mg(1)-O(3) | 177.43(14) |

| | | | |
|---|---|---|---|
| O(4)-Cs(1)#13 | 3.4852(3) | O(3)#5-Mg(1)-O(3) | 90.81(14) |
| O(4)-H(4A) | 0.830(10) | O(4)#8-Mg(1)-O(3)#8 | 177.43(14) |
| O(4)-H(4B) | 0.819(10) | O(4)#5-Mg(1)-O(3)#8 | 87.39(7) |
| P(1)-O(1) | 1.536(2) | O(4)-Mg(1)-O(3)#8 | 87.39(7) |
| P(1)-O(1)#7 | 1.536(2) | O(3)#5-Mg(1)-O(3)#8 | 90.81(14) |
| P(1)-O(1)#15 | 1.536(2) | O(3)-Mg(1)-O(3)#8 | 90.81(14) |
| P(1)-O(2) | 1.545(4) | O(4)#8-Mg(1)-Cs(1)#12 | 54.395(14) |
| O(4)#1-Cs(1)-O(4)#2 | 51.46(7) | O(4)#5-Mg(1)-Cs(1)#12 | 54.395(14) |
| O(4)#1-Cs(1)-O(4)#3 | 67.72(7) | O(4)-Mg(1)-Cs(1)#12 | 127.49(10) |
| O(4)#2-Cs(1)-O(4)#3 | 118.790(13) | O(3)#5-Mg(1)-Cs(1)#12 | 125.708(11) |
| O(4)#1-Cs(1)-O(4)#4 | 118.790(14) | O(3)-Mg(1)-Cs(1)#12 | 55.08(9) |
| O(4)#2-Cs(1)-O(4)#4 | 164.88(7) | O(3)#8-Mg(1)-Cs(1)#12 | 125.708(11) |
| O(4)#3-Cs(1)-O(4)#4 | 51.46(7) | O(4)#8-Mg(1)-Cs(1)#13 | 54.395(14) |
| O(4)#1-Cs(1)-O(4) | 118.790(14) | O(4)#5-Mg(1)-Cs(1)#13 | 127.49(10) |
| O(4)#2-Cs(1)-O(4) | 67.72(7) | O(4)-Mg(1)-Cs(1)#13 | 54.395(14) |
| O(4)#3-Cs(1)-O(4) | 164.88(7) | O(3)#5-Mg(1)-Cs(1)#13 | 55.08(9) |
| O(4)#4-Cs(1)-O(4) | 118.790(13) | O(3)-Mg(1)-Cs(1)#13 | 125.708(11) |
| O(4)#1-Cs(1)-O(4)#5 | 164.88(7) | O(3)#8-Mg(1)-Cs(1)#13 | 125.708(11) |
| O(4)#2-Cs(1)-O(4)#5 | 118.790(14) | Cs(1)#12-Mg(1)-Cs(1)#13 | 108.54(3) |
| O(4)#3-Cs(1)-O(4)#5 | 118.790(14) | O(4)#8-Mg(1)-Cs(1) | 127.49(10) |
| O(4)#4-Cs(1)-O(4)#5 | 67.72(7) | O(4)#5-Mg(1)-Cs(1) | 54.395(14) |
| O(4)-Cs(1)-O(4)#5 | 51.46(7) | O(4)-Mg(1)-Cs(1) | 54.395(14) |
| O(4)#1-Cs(1)-O(3)#6 | 48.45(5) | O(3)#5-Mg(1)-Cs(1) | 125.708(11) |
| O(4)#2-Cs(1)-O(3)#6 | 48.45(5) | O(3)-Mg(1)-Cs(1) | 125.708(11) |
| O(4)#3-Cs(1)-O(3)#6 | 87.80(4) | O(3)#8-Mg(1)-Cs(1) | 55.08(9) |
| O(4)#4-Cs(1)-O(3)#6 | 116.65(5) | Cs(1)#12-Mg(1)-Cs(1) | 108.54(3) |
| O(4)-Cs(1)-O(3)#6 | 87.80(4) | Cs(1)#13-Mg(1)-Cs(1) | 108.54(3) |
| O(4)#5-Cs(1)-O(3)#6 | 116.65(5) | O(4)#8-Mg(1)-Cs(1)#14 | 122.12(8) |
| O(4)#1-Cs(1)-O(3)#7 | 87.80(4) | O(4)#5-Mg(1)-Cs(1)#14 | 122.12(8) |
| O(4)#2-Cs(1)-O(3)#7 | 116.65(5) | O(4)-Mg(1)-Cs(1)#14 | 122.12(8) |
| O(4)#3-Cs(1)-O(3)#7 | 48.45(5) | O(3)#5-Mg(1)-Cs(1)#14 | 55.31(10) |
| O(4)#4-Cs(1)-O(3)#7 | 48.45(5) | O(3)-Mg(1)-Cs(1)#14 | 55.31(10) |
| O(4)-Cs(1)-O(3)#7 | 116.65(5) | O(3)#8-Mg(1)-Cs(1)#14 | 55.31(10) |
| O(4)#5-Cs(1)-O(3)#7 | 87.80(4) | Cs(1)#12-Mg(1)-Cs(1)#14 | 110.39(2) |
| O(3)#6-Cs(1)-O(3)#7 | 68.22(6) | Cs(1)#13-Mg(1)-Cs(1)#14 | 110.39(2) |
| O(4)#1-Cs(1)-O(3)#8 | 116.65(5) | Cs(1)-Mg(1)-Cs(1)#14 | 110.39(2) |
| O(4)#2-Cs(1)-O(3)#8 | 87.80(4) | Mg(1)-O(3)-Cs(1)#12 | 95.67(11) |
| O(4)#3-Cs(1)-O(3)#8 | 116.65(5) | Mg(1)-O(3)-Cs(1)#14 | 97.14(11) |
| O(4)#4-Cs(1)-O(3)#8 | 87.80(4) | Cs(1)#12-O(3)-Cs(1)#14 | 167.19(7) |
| O(4)-Cs(1)-O(3)#8 | 48.45(5) | Mg(1)-O(3)-H(3) | 122(3) |
| O(4)#5-Cs(1)-O(3)#8 | 48.45(5) | Cs(1)#12-O(3)-H(3) | 90(4) |
| O(3)#6-Cs(1)-O(3)#8 | 68.22(6) | Cs(1)#14-O(3)-H(3) | 83(4) |
| O(3)#7-Cs(1)-O(3)#8 | 68.22(6) | Mg(1)-O(4)-Cs(1)#13 | 96.84(4) |
| O(4)#1-Cs(1)-O(3)#9 | 97.53(3) | Mg(1)-O(4)-Cs(1) | 96.84(4) |

| | | | |
|---|---|---|---|
| O(4)#2-Cs(1)-O(3)#9 | 118.61(4) | Cs(1)#13-O(4)-Cs(1) | 164.88(7) |
| O(4)#3-Cs(1)-O(3)#9 | 71.62(5) | Mg(1)-O(4)-H(4A) | 116(3) |
| O(4)#4-Cs(1)-O(3)#9 | 71.62(5) | Cs(1)#13-O(4)-H(4A) | 89.9(3) |
| O(4)-Cs(1)-O(3)#9 | 118.61(4) | Cs(1)-O(4)-H(4A) | 89.9(3) |
| O(4)#5-Cs(1)-O(3)#9 | 97.53(3) | Mg(1)-O(4)-H(4B) | 130(3) |
| O(3)#6-Cs(1)-O(3)#9 | 145.63(2) | Cs(1)#13-O(4)-H(4B) | 83.14(14) |
| O(3)#7-Cs(1)-O(3)#9 | 112.093(12) | Cs(1)-O(4)-H(4B) | 83.14(15) |
| O(3)#8-Cs(1)-O(3)#9 | 145.63(2) | H(4A)-O(4)-H(4B) | 114.2(19) |
| O(4)#1-Cs(1)-O(3)#10 | 71.62(5) | O(1)-P(1)-O(1)#7 | 110.14(10) |
| O(4)#2-Cs(1)-O(3)#10 | 71.62(5) | O(1)-P(1)-O(1)#15 | 110.14(10) |
| O(4)#3-Cs(1)-O(3)#10 | 97.53(3) | O(1)#7-P(1)-O(1)#15 | 110.14(10) |
| O(4)#4-Cs(1)-O(3)#10 | 118.61(4) | O(1)-P(1)-O(2) | 108.80(10) |
| O(4)-Cs(1)-O(3)#10 | 97.53(3) | O(1)#7-P(1)-O(2) | 108.80(10) |
| O(4)#5-Cs(1)-O(3)#10 | 118.61(4) | O(1)#15-P(1)-O(2) | 108.80(10) |

Symmetry transformations used to generate equivalent atoms:

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

Table S7. Contribution of Different Geometrical Factors (g) for Structure Factors (C) in $RbMgPO_4{\cdot}6H_2O$ and $CsMgPO_4{\cdot}6H_2O$

| Crystals (n) | $g_{113}/n$ | $g_{223}/n$ | $g_{311}/n$ | $g_{322}/n$ | $g_{333}/n$ |
|---|---|---|---|---|---|
| $RbMgPO_4{\cdot}6H_2O$ (n = 2) | 0.355 | 0.449 | 0.355 | 0.449 | 0.803 |
| $CsMgPO_4{\cdot}6H_2O$ (n = 2) | 0 | 0 | 0.499 | 0 | 1.000 |

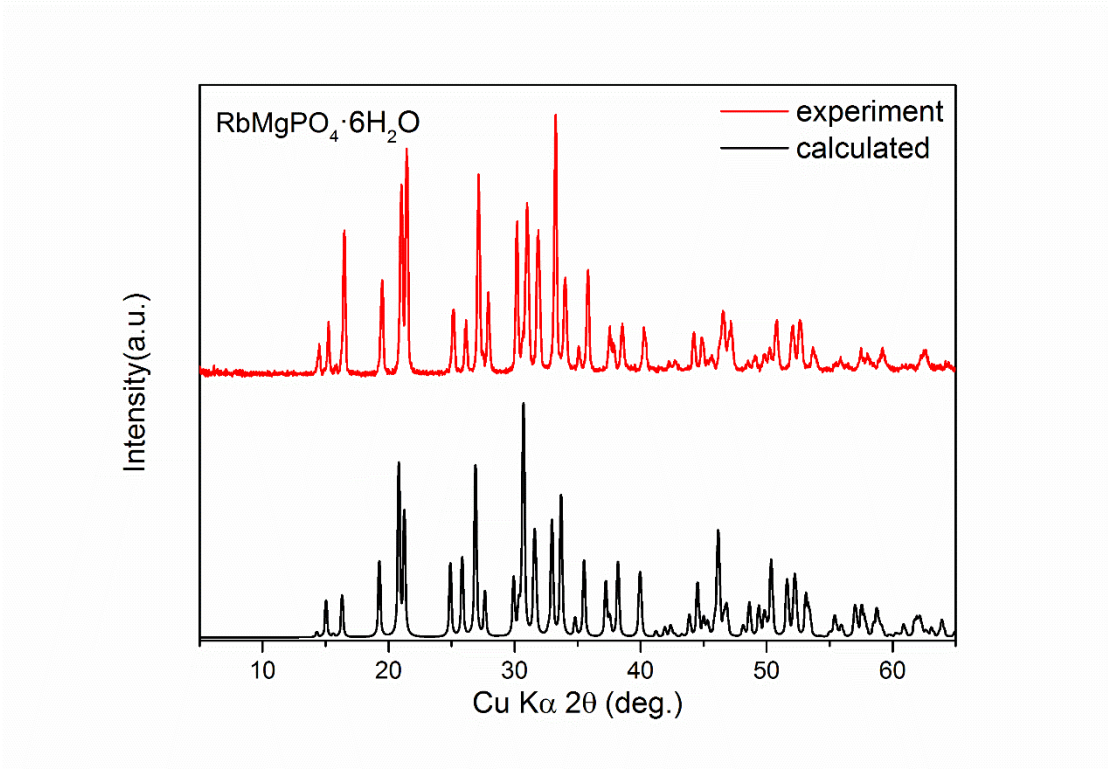
Table S8. Direction and magnitude of $MgO_6$ octahedra in $RbMgPO_4{\cdot}6H_2O$

| species | $U_x/D$ | $U_y/D$ | $U_z/D$ | $U_t/D$ |
|---|---|---|---|---|
| $Mg(1)O_6$ | 0.0000 | 0.1955 | 1.9888 | 1.9984 |
| $Mg(1)O_6$ | 0.0000 | -0.1955 | 1.9888 | 1.9984 |
| $MgO_6$ (in unit cell) | 0.0000 | 0.0000 | 3.9776 | 3.9776 |

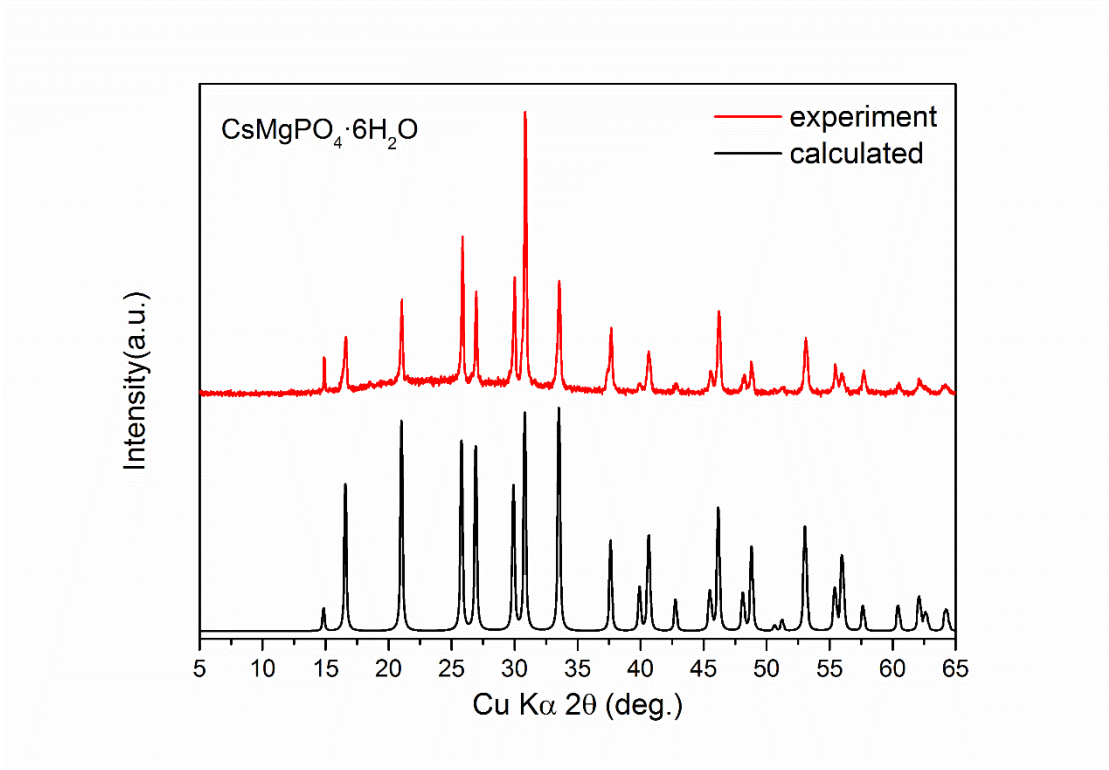
Table S9. Direction and magnitude of $MgO_6$ octahedra in $CsMgPO_4{\cdot}6H_2O$

| species | $U_x/D$ | $U_y/D$ | $U_z/D$ | $U_t/D$ |
|---|---|---|---|---|
| $Mg(1)O_6$ | 0.0000 | 0.0018 | -2.8776 | 2.8776 |
| $Mg(2)O_6$ | 0.0000 | -0.0019 | -2.8776 | 2.8776 |
| $MgO_6$ (in unit cell) | 0.0000 | -0.0001 | -5.7552 | 5.7552 |

Figure S1. Experimental and calculated Powder XRD patterns for $RbMgPO_4 \cdot 6H_2O$ (a) and $CsMgPO_4 \cdot 6H_2O$ (b)

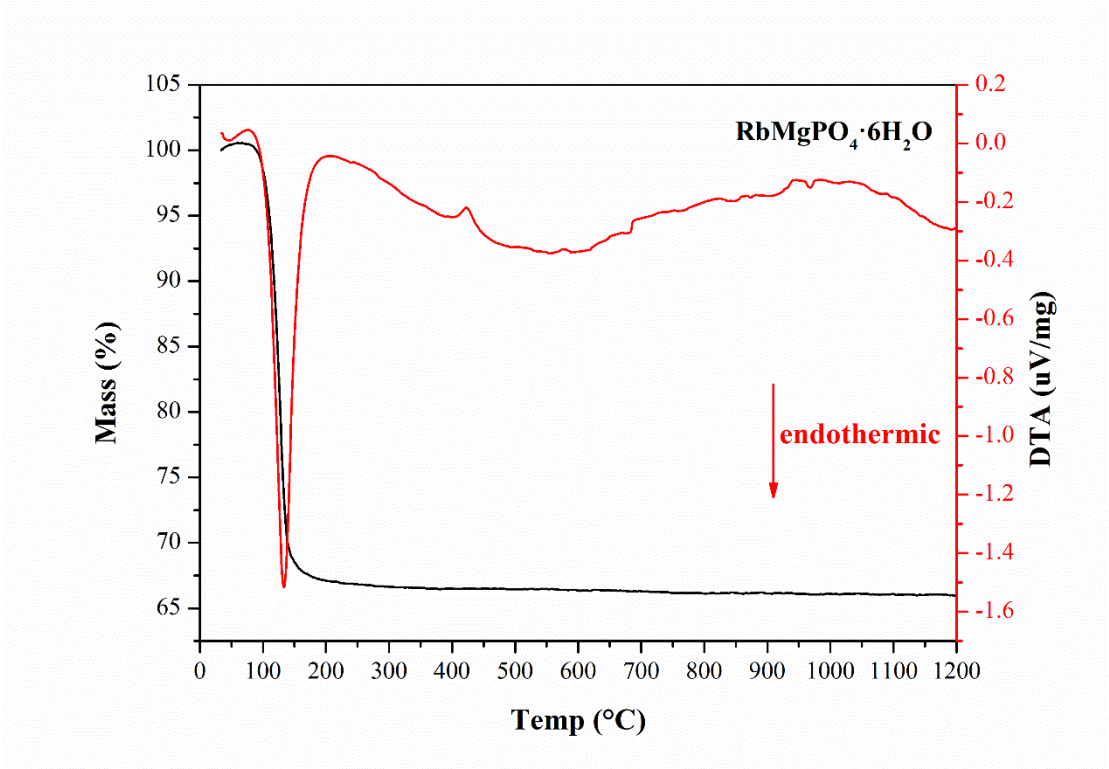



(a)

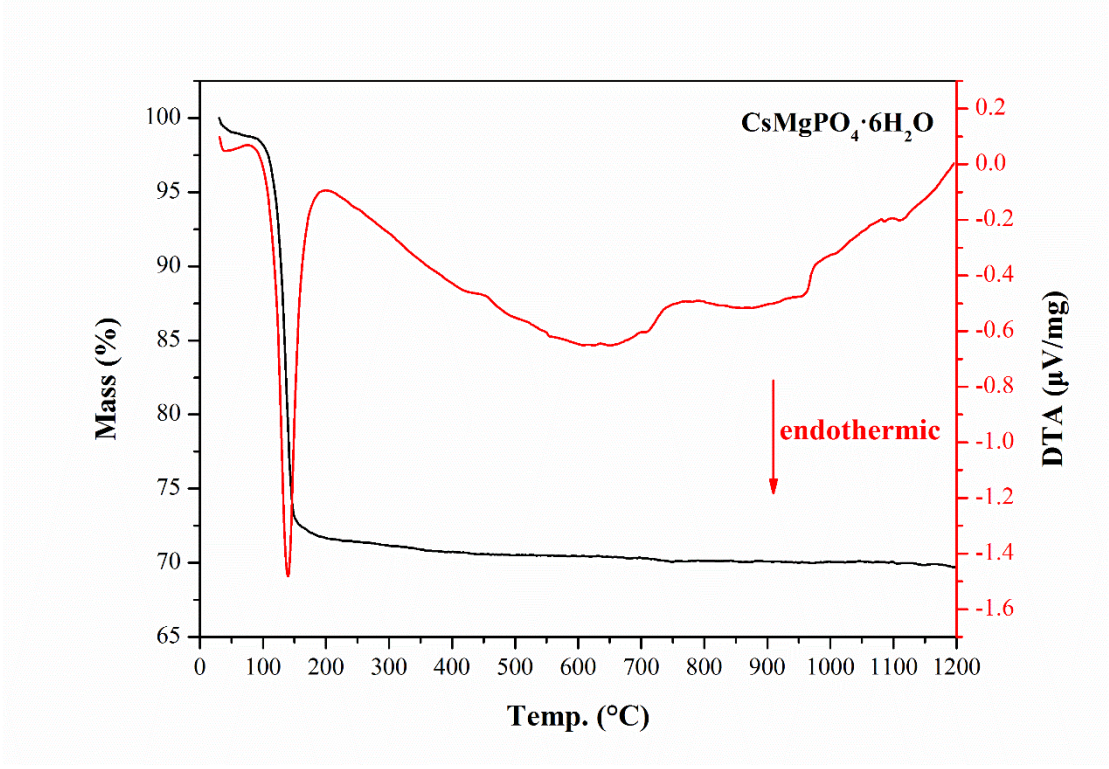



(b)

Figure S2. Thermogravimetric analysis curves for $RbMgPO_4 \cdot 6H_2O$ (a) and $CsMgPO_4 \cdot 6H_2O$ (b)

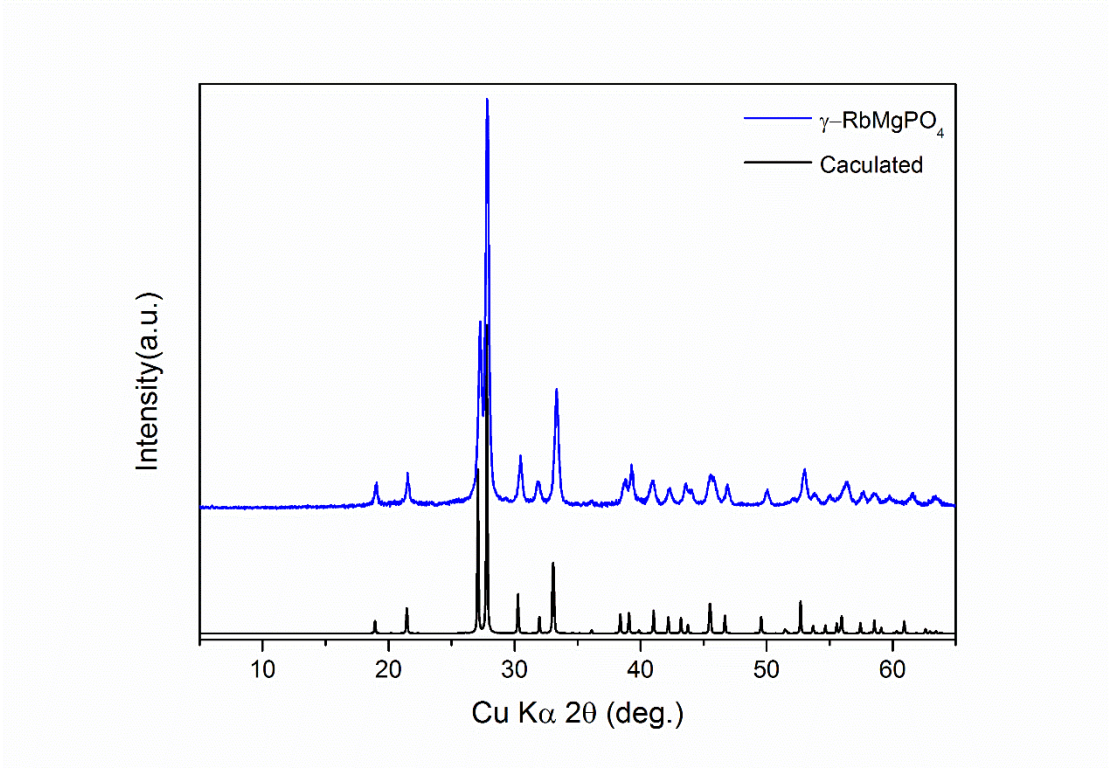



(a)

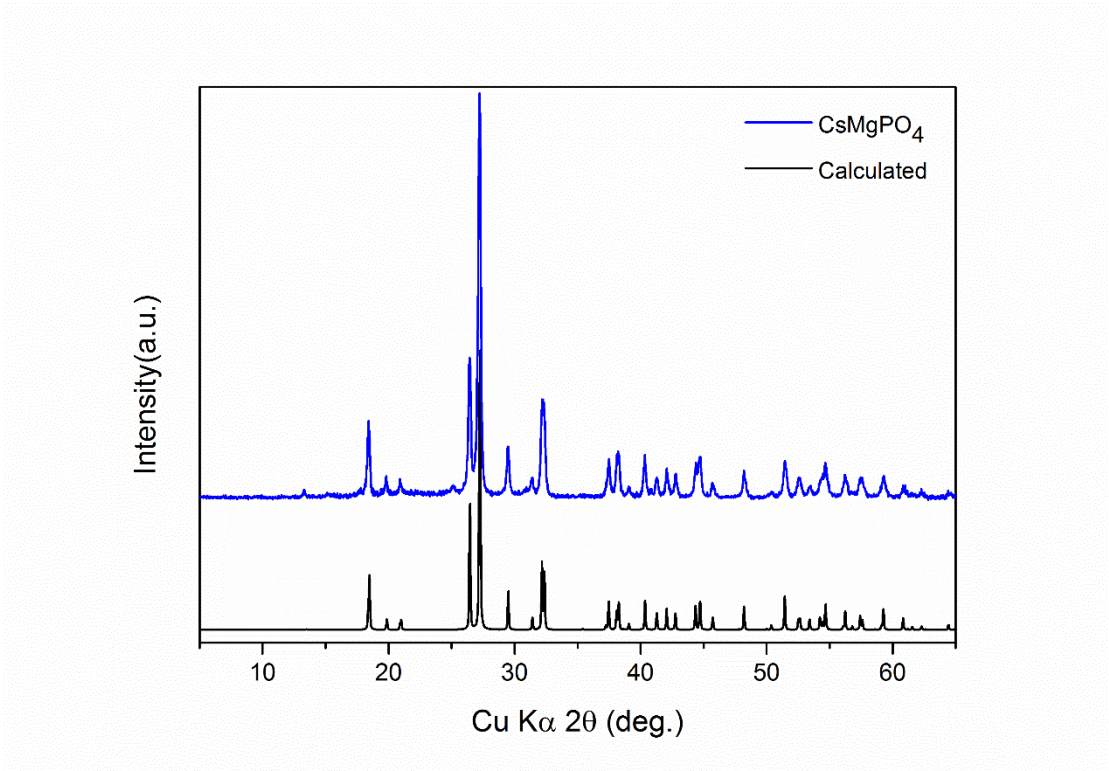



(b)

Figure S3. Powder X-ray diffraction for $RbMgPO_4 \cdot 6H_2O$ (a) and $CsMgPO_4 \cdot 6H_2O$ (b) at 160 ℃




(a)




(b)

Figure S4. Oscilloscope traces showing different SHG intensities for $RbMgPO_4 \cdot 6H_2O$ and $CsMgPO_4 \cdot 6H_2O$