Electronic Supplementary Material (ESI) for Dalton Transactions.

Effect of Cation Size on the Framework Structures of Magnesium Tungstate, $A_4Mg(WO_4)_3$ (A = Na, K), $R_2Mg_2(WO_4)_3$ (R = Rb, Cs)

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Table S1. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $Na_4Mg(WO_4)_3$, $K_4Mg(WO_4)_3$, $Rb_2Mg_2(WO_4)_3$ and $Cs_2Mg_2(WO_4)_3$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	$U_{(eq)}$	OCC (<1)	BVS
			$Na_4Mg(WO_4)_3$			
W(1)	5000	7872(1)	2500	21(1)		6.10
W(2)	7721(1)	1101(1)	3779(1)	21(1)		6.03
Na(1)	5000	0	0	45(1)		0.72
Na(2)	5000	7705(2)	-2500	20(1)		1.17
Na(3)	0	200(30)	7500	55(5)	0.45	0.62
Na(4)	0	9800(30)	7500	55(5)	0.55	0.66
Mg(1)	2897(2)	6579(2)	1230(3)	18(1)	0.5	1.72
Na(5)	2897(2)	6579(2)	1230(3)	18(1)	0.5	
O(1)	6268(4)	858(3)	3170(7)	30(1)		2.00
O(2)	4625(4)	7150(3)	292(6)	28(1)		2.02
O(3)	8310(4)	1706(3)	6103(6)	31(1)		2.12
O(4)	7848(4)	1809(3)	1784(7)	37(1)		1.92
O(5)	8486(4)	9974(3)	4024(7)	39(1)		2.26
O(6)	3912(4)	8690(3)	2445(8)	44(1)		2.03
			$K_4Mg(WO_4)_3$			
W(1)	8782(1)	3563(1)	1860(1)	19(1)		6.17
W(2)	7625(1)	-1886(1)	2558(1)	20(1)		6.04
W(3)	3811(1)	1497(1)	3887(1)	27(1)		5.96
K(1)	3513(3)	4325(2)	1129(2)	27(1)		1.32
K(2)	0	0	0	32(1)		1.09
K(3)	2204(3)	7615(2)	2239(2)	24(1)		1.16
K(4)	2551(3)	4792(2)	5264(2)	35(1)		0.86
K(5)	5000	0	0	39(1)		0.83
Mg(1)	8431(5)	1219(3)	4479(3)	37(1)		1.96
O(1)	7566(8)	-90(6)	2683(6)	27(1)		2.00
O(2)	5538(9)	-3080(7)	2680(6)	32(2)		1.91
O(3)	3890(8)	3248(7)	3676(6)	32(1)		2.14
O(4)	921(9)	4880(7)	2096(7)	36(2)		2.13

O(5)	9645(8)	-2212(7)	3715(6)	30(1)	2.07
O(6)	6114(9)	1502(7)	4916(7)	38(2)	2.02
O(7)	8871(10)	3000(8)	3531(7)	43(2)	1.83
O(8)	8443(9)	2162(8)	563(7)	42(2)	2.05
O(9)	3216(9)	525(7)	2217(6)	33(2)	1.94
O(10)	8017(10)	-750(8)	5337(8)	48(2)	1.63
O(11)	7760(10)	-2189(8)	869(8)	49(2)	2.09
O(12)	6964(11)	4346(9)	1355(8)	52(2)	2.00
			$Rb_2Mg_2(WO_4)_3$		
W(1)	7757(1)	6269(1)	507(1)	10(1)	6.25
Rb(1)	7950(1)	2950(1)	2050(1)	41(1)	0.63
Rb(2)	4294(1)	5706(1)	706(1)	24(1)	0.86
Mg(1)	1360(2)	1360(2)	1360(2)	12(1)	2.20
Mg(2)	5875(2)	9125(2)	875(2)	11(1)	2.22
O(1)	9285(5)	6478(7)	-15(6)	39(2)	2.03
O(2)	6962(6)	5162(7)	-387(6)	43(2)	2.08
O(3)	6992(7)	7676(7)	291(8)	54(2)	2.11
O(4)	7683(8)	5784(7)	2065(5)	49(2)	2.00
			$Cs_2Mg_2(WO_4)_3$		
W(1)	1984(1)	8760(1)	9743(1)	8(1)	6.11
Cs(1)	417(1)	5417(1)	9583(1)	26(1)	0.84
Cs(2)	3220(1)	1780(1)	8220(1)	17(1)	1.16
Mg(1)	-1138(2)	8863(2)	8863(2)	9(1)	2.11
Mg(2)	3370(2)	8370(2)	6630(2)	9(1)	2.07
O(1)	2510(4)	8966(4)	8220(4)	19(1)	2.00
O(2)	2217(4)	150(4)	533(4)	21(1)	2.07
O(3)	431(4)	8286(4)	9804(4)	20(1)	2.00
O(4)	2859(4)	7628(4)	509(4)	20(1)	1.72

Table S2. Selected bond lengths (Å) and angles (deg.) for $Na_4Mg(WO_4)_3$.

W(1)-O(6)#1	1.756(5)	Na(2)-O(2)	2.353(4)
W(1)-O(6)	1.756(5)	Na(2)-O(3)#9	2.408(4)
W(1)-O(2)	1.774(4)	Na(2)-O(3)#10	2.408(4)
W(1)-O(2)#1	1.774(4)	Na(2)-O(1)#7	2.457(5)
W(2)-O(1)	1.748(4)	Na(2)-O(1)#6	2.457(5)
W(2)-O(3)	1.759(4)	Na(4)-O(5)#11	2.524(6)
W(2)-O(4)	1.785(5)	Na(4)-O(5)	2.524(6)
W(2)-O(5)	1.786(4)	Na(4)-O(5)#4	2.550(7)
Na(1)-O(1)	2.527(4)	Na(4)-O(5)#13	2.550(7)
Na(1)-O(1)#6	2.527(4)	Mg(1)-O(6)#3	2.146(6)
Na(1)-O(6)#7	2.559(5)	Mg(1)-O(3)#9	2.174(5)
Na(1)-O(6)#1	2.559(5)	Mg(1)-O(2)	2.182(5)
Na(1)-O(1)#7	2.688(5)	Mg(1)-O(4)#15	2.212(5)
Na(1)-O(1)#1	2.688(5)	Mg(1)-O(5)#16	2.226(5)
Na(2)-O(2)#8	2.353(4)	Mg(1)-O(4)#6	2.362(5)
O(6)#1-W(1)-O(6)	101.2(4)	O(3)#9-Na(2)-O(3)#10	111.2(2)
O(6)#1-W(1)-O(2)	108.4(2)	O(2)#8-Na(2)-O(1)#7	95.71(16)
O(6)-W(1)-O(2)	112.8(2)	O(2)#8-Na(2)-O(1)#6	114.37(16)
O(1)-W(2)-O(3)	110.9(2)	O(2)-Na(2)-O(1)#6	95.71(16)
O(1)-W(2)-O(4)	107.6(2)	O(3)#9-Na(2)-O(1)#6	87.66(15)
O(3)-W(2)-O(4)	112.1(2)	O(3)#10-Na(2)-O(1)#6	160.19(17)
O(1)-W(2)-O(5)	109.8(2)	O(1)#7-Na(2)-O(1)#6	74.5(2)
O(3)-W(2)-O(5)	106.8(2)	O(6)#3-Mg(1)-O(3)#9	102.9(2)
O(1)-Na(1)-O(1)#6	180.000(1)	O(6)#3-Mg(1)-O(2)	166.88(19)
O(1)-Na(1)-O(6)#7	108.22(15)	O(3)#9-Mg(1)-O(2)	83.67(17)
O(1)#6-Na(1)-O(6)#7	71.78(15)	O(6)#3-Mg(1)-O(4)#15	90.5(2)
O(1)#6-Na(1)-O(1)#7	69.45(17)	O(3)#9-Mg(1)-O(4)#15	162.9(2)
O(6)#7-Na(1)-O(1)#7	102.06(17)	O(2)-Mg(1)-O(4)#15	81.19(18)
O(6)#1-Na(1)-O(1)#7	77.94(17)	O(2)-Mg(1)-O(5)#16	93.32(18)
O(2)#8-Na(2)-O(2)	142.5(3)	O(4)#15-Mg(1)-O(5)#16	100.69(19)
O(2)#8-Na(2)-O(3)#9	83.78(16)	O(6)#3-Mg(1)-O(4)#6	78.16(18)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, y, -z+1/2 #2 x+1/2, -y+3/2, z+1/2 #3 -x+1/2, -y+3/2, -z #4 -x+2, -y+2, -z+1
#5 x+1/2, y+1/2, z+1 #6 -x+1, -y+2, -z #7 x, -y+2, z-1/2 #8 -x+1, y, -z-1/2
#9 x-1/2, y-1/2, z-1 #10 -x+3/2, y-1/2, -z+1/2 #11 -x+2, y, -z+3/2 #12 -x+2, -y+2, -z+2
#13 x, -y+2, z+1/2 #14 -x+3/2, -y+3/2, -z+1 #15 x-1/2, y-1/2, z #16 x-1/2, -y+3/2, z-1/2
#17 x+1/2, y+1/2, z

Table S3. Selected bond lengths (Å) and angles (deg.) for $K_4Mg(WO_4)_3$.

W(1)-O(4)	1.749(7)	K(3)-O(8)#3	2.745(7)
W(1)-O(12)	1.750(7)	K(3)-O(6)#2	2.755(7)
W(1)-O(8)	1.759(7)	K(3)-O(2)#9	2.766(6)
W(1)-O(7)	1.786(7)	K(3)-O(9)#9	2.779(7)
W(2)-O(11)	1.743(7)	K(3)-O(5)#12	2.822(6)
W(2)-O(2)	1.762(6)	K(4)-O(3)	2.735(6)
W(2)-O(5)	1.779(6)	K(4)-O(3)#2	2.766(7)
W(2)-O(1)	1.792(6)	K(4)-O(7)#8	2.888(7)
W(3)-O(3)	1.747(6)	K(4)-O(7)#2	3.037(7)
W(3)-O(9)	1.756(6)	K(4)-O(2)#4	3.055(7)
W(3)-O(6)	1.782(6)	K(4)-O(5)#4	3.066(7)
W(3)-O(10)#4	1.811(7)	K(4)-O(4)#8	3.084(7)
K(1)-O(11)#7	2.594(8)	K(5)-O(8)	2.809(7)
K(1)-O(12)	2.605(8)	K(5)-O(8)#7	2.809(7)
K(1)-O(4)#8	2.628(6)	K(5)-O(1)#7	2.874(6)
K(1)-O(2)#9	2.730(7)	K(5)-O(1)	2.874(6)
K(1)-O(3)	2.796(7)	K(5)-O(9)	3.023(6)
K(1)-O(12)#3	2.864(8)	K(5)-O(9)#7	3.023(6)
K(2)-O(9)#10	2.720(6)	Mg(1)-O(5)#13	1.982(7)
K(2)-O(9)	2.720(6)	Mg(1)-O(1)	1.989(6)
K(2)-O(11)#7	2.738(8)	Mg(1)-O(6)	2.046(7)
K(2)-O(11)#8	2.738(8)	Mg(1)-O(7)	2.047(8)
K(2)-O(8)#8	2.831(7)	Mg(1)-O(10)	2.159(8)
K(2)-O(8)#7	2.831(7)	Mg(1)-O(10)	2.862
K(3)-O(4)#8	2.601(7)		
O(4)-W(1)-O(12)	107.4(3)	O(9)#10-K(2)-O(9)	180.0(2)
O(11)-W(2)-O(2)	109.3(3)	O(9)#10-K(2)-O(11)#8	81.9(2)
O(11)-W(2)-O(5)	106.1(3)	O(6)#2-K(3)-O(2)#9	78.94(19)
O(3)-W(3)-O(9)	108.2(3)	O(11)#7-K(2)-O(11)#8	180.0(3)
O(3)-W(3)-O(6)	107.8(3)	O(11)#7-K(2)-O(8)#7	99.1(2)
O(9)-W(3)-O(6)	109.5(3)	O(11)#8-K(2)-O(8)#7	80.9(2)
O(11)#7-K(1)-O(12)	89.6(2)	O(8)#3-K(3)-O(6)#2	155.7(2)
O(4)#8-K(1)-O(2)#9	80.1(2)	O(8)#3-K(3)-O(2)#9	96.90(19)
O(12)-K(1)-O(3)	88.8(2)	O(4)#8-K(3)-O(9)#9	174.2(2)
O(4)#8-K(1)-O(3)	73.79(19)	O(6)#2-K(3)-O(11)#12	116.28(19)
O(11)#7-K(1)-O(12)#3	77.1(2)	O(9)#9-K(3)-O(11)#12	83.44(19)

Symmetry transformations used to generate equivalent atoms:

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

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

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

Table S4. Selected bond lengths (Å) and angles (deg.) for $Rb_2Mg_2(WO_4)_3$.

W(1)-O(3)	1.739(7)	Rb(2)-O(3)#8	3.213(8)
W(1)-O(1)	1.753(6)	Rb(2)-O(3)#9	3.213(8)
W(1)-O(2)	1.755(6)	Rb(2)-O(3)#10	3.213(8)
W(1)-O(4)	1.759(5)	Rb(2)-O(3)#11	3.624(8)
Rb(1)-O(4)#3	3.065(8)	Rb(2)-O(3)	3.624(8)
Rb(1)-O(4)#4	3.065(8)	Rb(2)-O(3)#6	3.624(8)
Rb(1)-O(4)	3.065(8)	Mg(1)-O(2)#12	2.050(7)
Rb(1)-O(2)#5	3.428(7)	O(2)-Mg(1)#20	2.050(7)
Rb(1)-O(2)#6	3.428(7)	Mg(1)-O(2)#7	2.050(7)
Rb(1)-O(2)#7	3.428(7)	Mg(1)-O(4)#13	2.078(7)
Rb(1)-O(3)#7	3.554(8)	Mg(1)-O(4)#3	2.078(7)
Rb(1)-O(3)#5	3.554(8)	Mg(1)-O(4)#14	2.078(7)
Rb(1)-O(3)#6	3.554(8)	Mg(2)-O(1)#15	2.052(6)
Rb(2)-O(1)#8	3.121(8)	Mg(2)-O(1)#16	2.052(6)
Rb(2)-O(1)#9	3.121(8)	Mg(2)-O(1)#9	2.052(6)
Rb(2)-O(1)#10	3.121(8)	Mg(2)-O(3)#17	2.068(7)
Rb(2)-O(2)#11	3.159(7)	Mg(2)-O(3)	2.068(7)
Rb(2)-O(2)#6	3.159(7)	Mg(2)-O(3)#8	2.068(7)
Rb(2)-O(2)	3.159(7)		
O(3)-W(1)-O(1)	106.8(4)	O(4)-Rb(1)-O(3)#5	100.67(16)
O(1)-W(1)-O(4)	112.7(3)	O(3)#7-Rb(1)-O(3)#5	80.5(2)
O(4)#3-Rb(1)-O(4)#4	95.62(19)	O(4)#3-Rb(1)-O(3)#6	163.68(19)
O(4)#4-Rb(1)-O(2)#5	148.96(19)	O(2)#7-Rb(1)-O(3)#6	126.99(17)
O(4)-Rb(1)-O(2)#5	53.70(15)	O(3)#7-Rb(1)-O(3)#6	80.5(2)
O(4)#3-Rb(1)-O(2)#6	148.96(19)	O(3)#5-Rb(1)-O(3)#6	80.5(2)
O(4)#4-Rb(1)-O(2)#6	53.70(15)	O(3)-Rb(2)-O(3)#6	116.25(7)
O(4)-Rb(1)-O(2)#6	84.27(18)	O(2)#12-Mg(1)-O(2)#4	90.3(3)
O(2)#5-Rb(1)-O(2)#6	118.89(4)	O(2)#12-Mg(1)-O(2)#7	90.3(3)
O(4)#3-Rb(1)-O(2)#7	53.70(15)	O(2)#4-Mg(1)-O(2)#7	90.3(3)
O(4)#4-Rb(1)-O(2)#7	84.27(18)	O(2)#12-Mg(1)-O(4)#13	89.2(3)
O(4)-Rb(1)-O(2)#7	148.96(19)	O(2)#4-Mg(1)-O(4)#13	91.2(2)
O(4)-Rb(1)-O(3)#7	163.68(19)	O(4)#13-Mg(1)-O(4)#3	89.3(3)
O(2)#5-Rb(1)-O(3)#7	126.99(17)	O(2)#12-Mg(1)-O(4)#14	91.2(2)
O(4)#4-Rb(1)-O(3)#5	163.68(19)	O(4)#3-Mg(1)-O(4)#14	89.3(3)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2, -y+3/2, -z #2 -x+3/2, -y+1, z-1/2 #3 y+1/2, -z+1/2, -x+1 #4 -z+1, x-1/2, -y+1/2
#5 -x+3/2, -y+1, z+1/2 #6 -z+1/2, -x+1, y-1/2 #7 -y+3/2, -z, x-1/2 #8 z+1/2, -x+3/2, -y+1
#9 x-1/2, -y+3/2, -z #10 y-1/2, -z+1/2, -x+1 #11 -y+1, z+1/2, -x+1/2 #12 x+1/2, -y+1/2, -z
#13 -z+3/2, -x+1, y-1/2 #14 -x+2, y-1/2, -z+1/2 #15 y, z+1, x-1 #16 -z+1/2, -x+2, y-1/2
#17 -y+3/2, -z+1, x-1/2 #18 -x+1, y+1/2, -z+1/2 #19 -x+2, y+1/2, -z+1/2 #20 x-1/2,-y+1/2,-z

Table S5. Selected bond lengths (Å) and angles (deg.) for $Cs_2Mg_2(WO_4)_3$.

W(1)-O(2)	1.758(4)	Cs(2)-O(4)#11	3.239(4)
W(1)-O(4)	1.765(4)	Cs(2)-O(4)#12	3.239(4)
W(1)-O(3)	1.767(4)	Cs(2)-O(2)#8	3.266(4)
W(1)-O(1)	1.768(4)	Cs(2)-O(2)	3.266(4)
Cs(1)-O(3)	3.131(4)	Cs(2)-O(2)#9	3.266(4)
Cs(1)-O(3)#3	3.131(4)	Cs(2)-O(2)#11	3.630(4)
Cs(1)-O(3)#4	3.131(4)	Cs(2)-O(2)#10	3.630(4)
Cs(1)-O(4)#5	3.503(4)	Cs(2)-O(2)#12	3.630(4)
Cs(1)-O(4)#6	3.503(4)	Mg(1)-O(4)#7	2.071(5)
Cs(1)-O(4)#7	3.503(4)	Mg(1)-O(4)#13	2.071(5)
Cs(1)-O(2)#7	3.538(4)	Mg(1)-O(4)#3	2.071(5)
Cs(1)-O(2)#6	3.538(4)	Mg(1)-O(3)#14	2.087(5)
Cs(1)-O(2)#5	3.538(4)	Mg(1)-O(3)	2.087(5)
Cs(1)-O(4)	3.723(4)	Mg(1)-O(3)#10	2.087(5)
Cs(1)-O(4)#3	3.723(4)	Mg(2)-O(1)#3	2.070(4)
Cs(1)-O(4)#4	3.723(4)	Mg(2)-O(1)	2.070(4)
Cs(2)-O(1)#8	3.157(5)	Mg(2)-O(1)#4	2.070(4)
Cs(2)-O(1)	3.157(5)	Mg(2)-O(2)#9	2.103(5)
Cs(2)-O(1)#9	3.157(5)	Mg(2)-O(2)#11	2.103(5)
Cs(2)-O(4)#10	3.239(4)	Mg(2)-O(2)#17	2.103(5)
O(2)-W(1)-O(4)	107.0(2)	O(2)#8-Cs(2)-O(2)#12	49.93(14)
O(2)#9-Cs(2)-O(2)#12	105.226(15)	O(2)-Cs(2)-O(2)#12	136.99(8)
O(1)-Cs(2)-O(2)#9	52.10(11)	O(2)#11-Cs(2)-O(2)#12	115.85(5)
O(4)#12-Cs(2)-O(2)#8	92.62(11)	O(4)#7-Mg(1)-O(3)	91.93(16)
O(1)#8-Cs(2)-O(2)	52.10(11)	O(4)#13-Mg(1)-O(3)	176.66(18)
O(1)-Cs(2)-O(2)	52.55(11)	O(4)#3-Mg(1)-O(3)	87.49(18)
O(1)#9-Cs(2)-O(2)	120.83(11)	O(3)#14-Mg(1)-O(3)	89.52(19)
O(4)#10-Cs(2)-O(2)	92.62(11)	O(4)#7-Mg(1)-O(3)#10	176.66(18)
O(4)#12-Cs(2)-O(2)	135.01(11)	O(4)#3-Mg(1)-O(3)#10	91.93(16)
O(2)#8-Cs(2)-O(2)	91.18(11)	O(3)#14-Mg(1)-O(3)#10	89.52(19)
O(1)#8-Cs(2)-O(2)#9	120.83(11)	O(3)-Mg(1)-O(3)#10	89.52(19)
O(1)#9-Cs(2)-O(2)#9	52.55(11)	O(1)#3-Mg(2)-O(1)	91.4(2)
O(4)#10-Cs(2)-O(2)#9	135.01(12)	O(1)#3-Mg(2)-O(1)#4	91.4(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2, -y+2, z+1/2 #2 x+1/2, -y+3/2, -z+2 #3 -z+1, x+1/2, -y+3/2 #4 y-1/2,-z+3/2,-x+1 #5 -y+1, z-1/2, -x+3/2 #6 z-1, x, y #7 x-1/2, -y+3/2, -z+2 #8 z-1/2, -x+3/2, -y+2 #9 -y+3/2, -z+2, x+1/2 #10 z-1, x+1, y #11 -x+1/2, -y+2, z-1/2 #12 y-1/2, -z+5/2, -x+1 #13 -y+1/2, -z+2, x+1/2 #14 y-1, z, x+1 #15 -x, y-1/2, -z+3/2 #16 -x, y+1/2, -z+3/2 #17 -z+3/2, -x+1, y-1/2 #18 -x+1, y-1/2, -z+3/2

Figure S1. Experimental and calculated XRD patterns of the $Na_4Mg(WO_4)_3$, $K_4Mg(WO_4)_3$, $Rb_2Mg_2(WO_4)_3$ and $Cs_2Mg_2(WO_4)_3$ crystals.

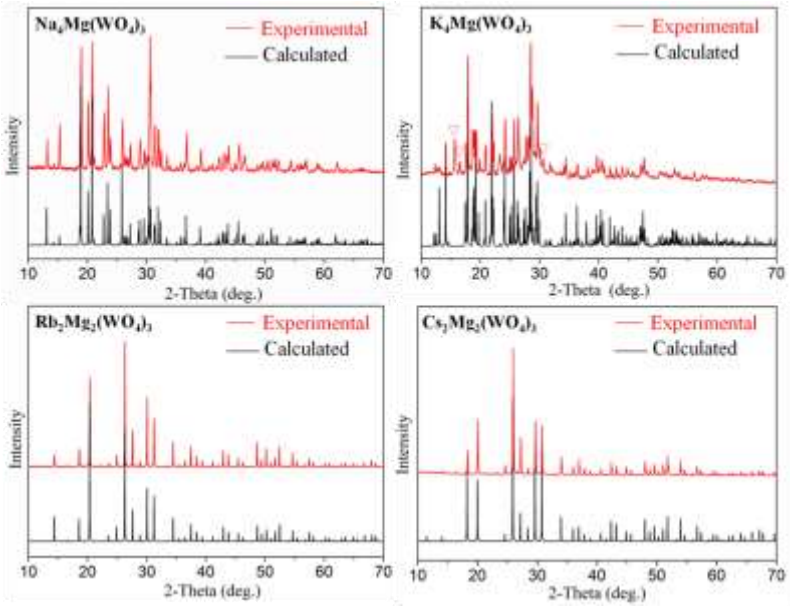


Figure S2. Coordination environments of the Na atoms in $Na_4Mg(WO_4)_3$.

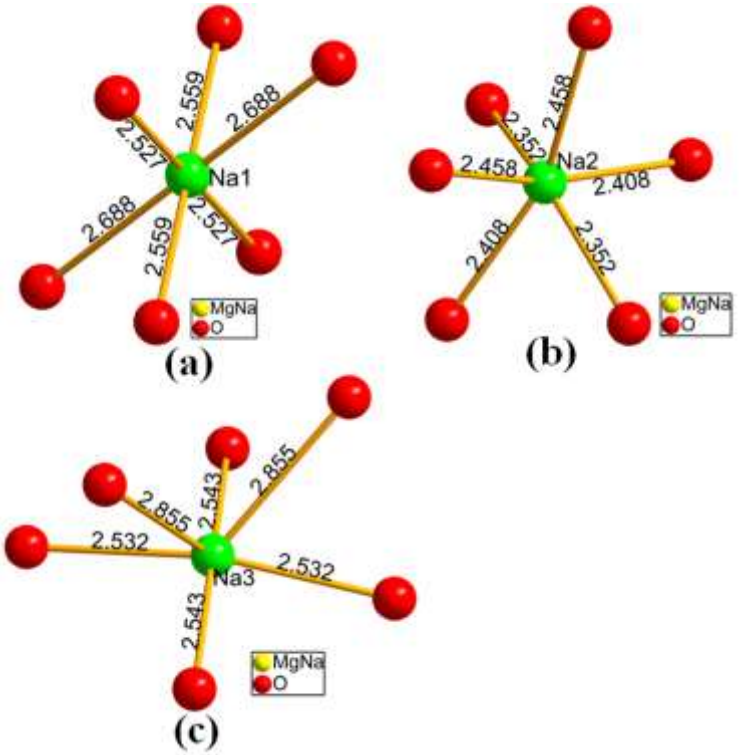


Figure S3. The $(Mg/Na)_2O_{10}$ dimers surrounded by eight WO_4 tetrahedra in $Na_4Mg(WO_4)_3$.

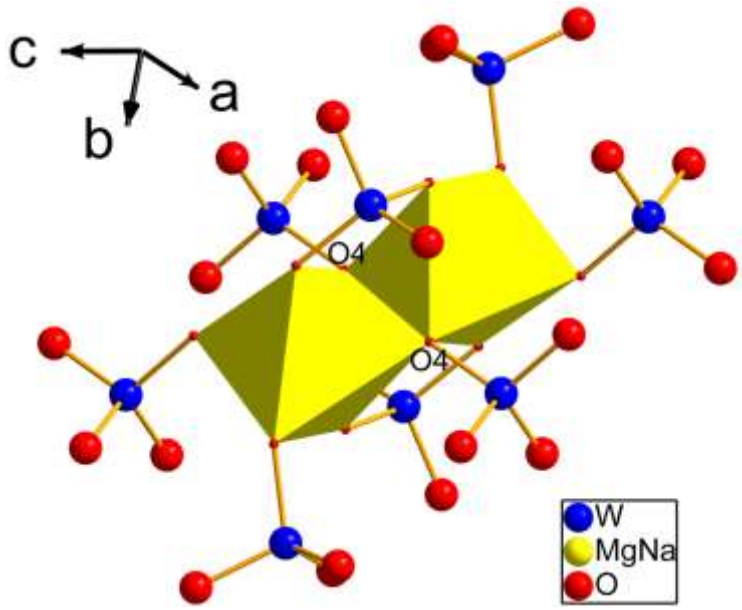


Figure S4. Coordination environments of the K atoms in $K_4Mg(WO_4)_3$.

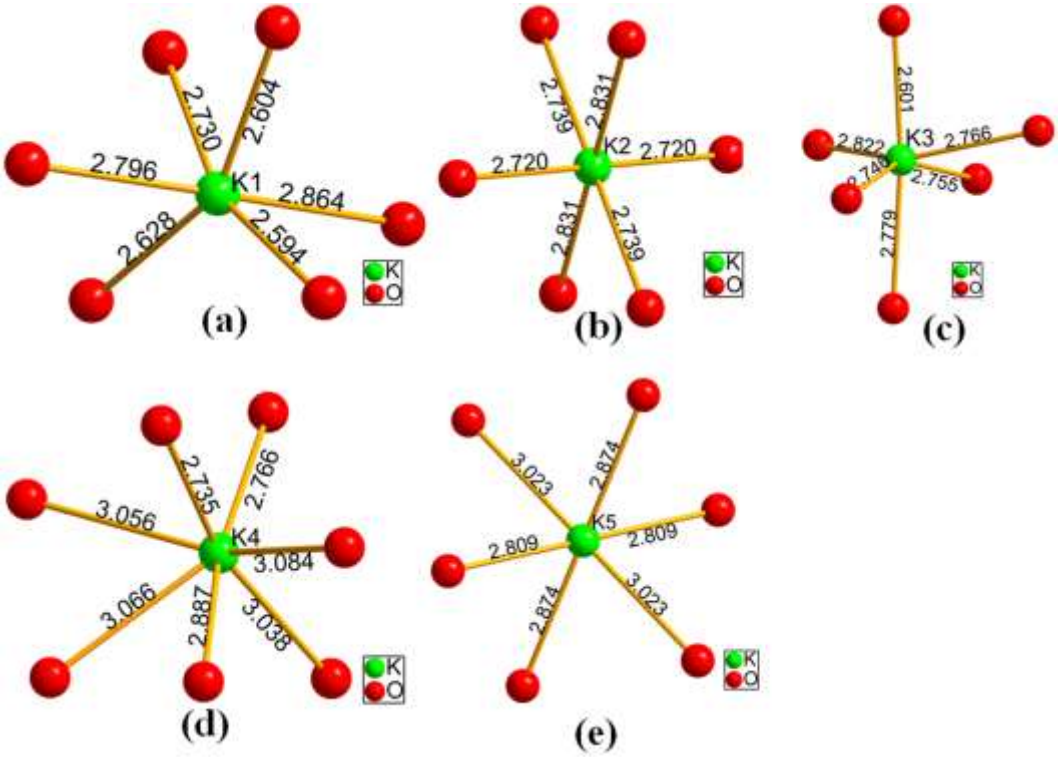


Figure S5. Coordination environments of the Cs and Rb atoms in $Cs_2Mg_2(WO_4)_3$ and $Rb_2Mg_2(WO_4)_3$, respectively.

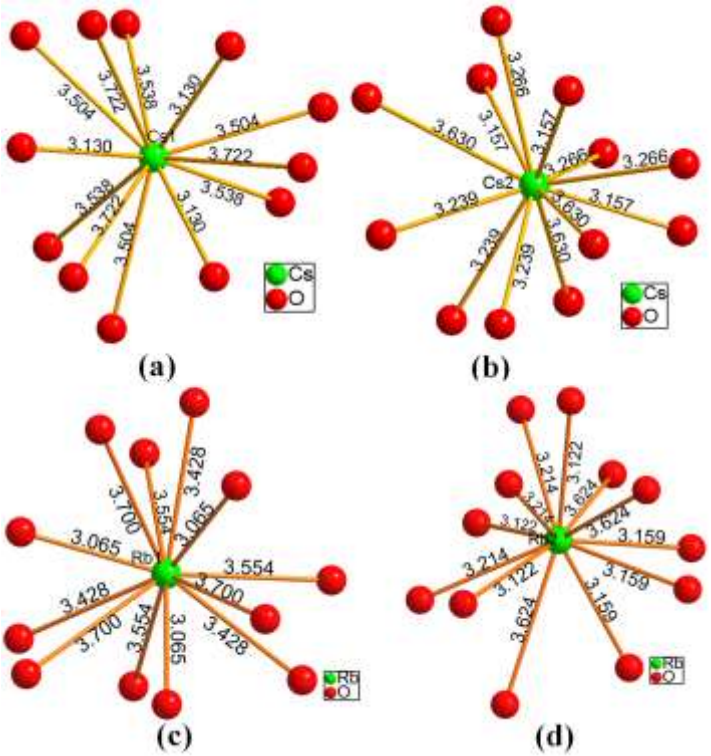


Figure S6. The infrared spectra of $Na_4Mg(WO_4)_3$, $K_4Mg(WO_4)_3$, $Rb_2Mg_2(WO_4)_3$ and $Cs_2Mg_2(WO_4)_3$.

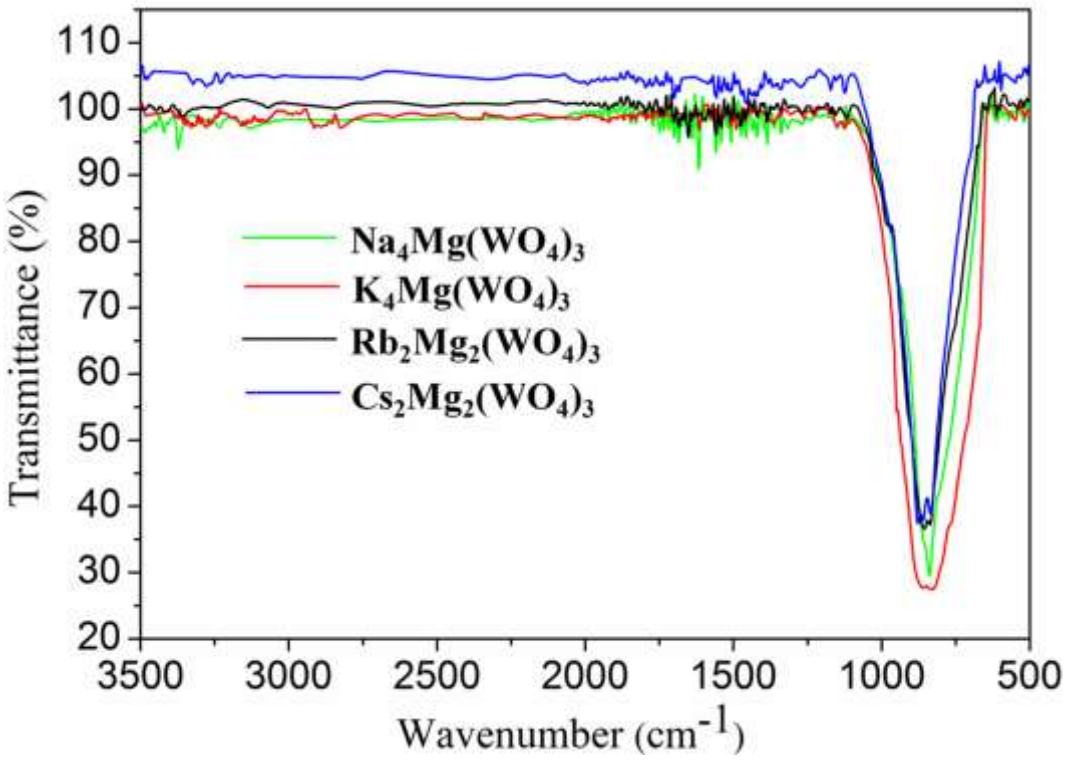


Figure S7. Phase matching curve, i.e., particle size vs SHG intensity, data for $Rb_2Mg_2(WO_4)_3$ and $Cs_2Mg_2(WO_4)_3$.

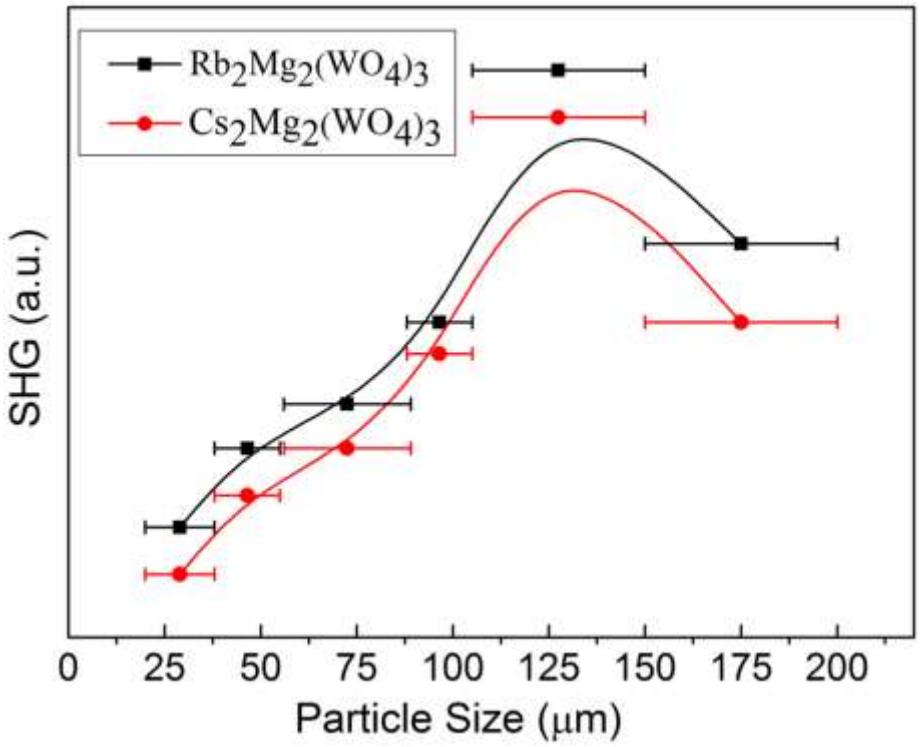
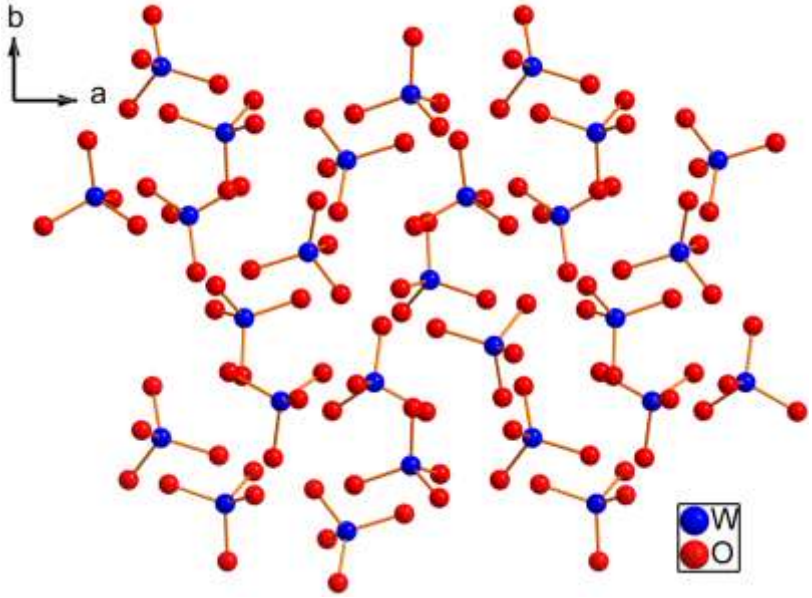


Figure S8. The arrangement of isolated WO_4 tetrahedra.



The explanations for the bandgap difference among the title compounds and the reported compounds, $Lu_6Mo(W)O_{12}$, $La_3BW_{1-x}Mo_xO_9$ and $Y_6W(Mo)O_{12}$

There are many materials whose bandgap are about 1.8 ~ 3.3 eV, smaller than that of the materials described in our manuscript, while there are also many materials whose bandgap are as large as that of the materials described in our manuscript. For example, the bandgap of $Rb_3Na(WO_4)_2$ and $Rb_3Na(MoO_4)_2$ are 5.01 eV and 4.84 eV, respectively.[1]

It is interesting to analyze the contribution of different cations to the bandgap. The bandgap of different compound is mainly determined by the covalent chemical bond whose electron states site nearby the forbidden bandgap. For example, for $Rb_3Na(WO_4)_2$,[1] the states at the top of valence band are mainly O-p states, while at the bottom of the conduction band there are mainly W-p and W-d states. Hence the bandgap of $Rb_3Na(WO_4)_2$ is determined by W-O. Once the alkali metal cations were substituted by lanthanide, the bandgap is determined by the covalent interaction between oxygen and lanthanide. For example, the bandgap of Lu_6WO_{12} is determined by Lu-O interaction (shown in Figure 5 in Ref. 2). Owing to the relativistic effect and the electron negativity, the bandgap of compound containing Lu is generally smaller than the one containing W.

1. C. Bai, C. Lei, S. Pan, Y. Wang, Z. Yang, S. Han, H. Yu, Y. Yang, F. Zhang, *Solid State Sci.* 2014, **33**, 32.

2. H. Li, H.K. Yang, B.K. Moon, B.C. Choi, J.H. Jeong, K. Jang, H.S. Lee, S.S. Yi, *Inorg. Chem.* 2011, **50**, 12522.