Electronic Supplementary Information

Exploring quaternary Vanadates Containing Alkali, Alkaline Earth Metal, and [VO_4] in Quest for Nonlinear Optical Materials

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Experimental Procedures

Single-Crystal X-ray Diffraction

Single crystal XRD data were collected at room temperature using a Bruker D8 Venture diffractometer and Mo Kα radiation (λ =0.71073 Å) and data integration, cell refinement, and absorption correction were performed using the SAINT and SADABS programs. The structure was solved by direct methods and refined by full matrix least-squares techniques on F^2 using the SHELXT and SHELXL program implemented in Olex2.[1] PLATON was used to examine the possible higher symmetry of the structure, and the result shows that no higher symmetry are existed.[2] Detailed information on the structural data is given in Table S1 and S2, the redefined atomic positions, equivalent isotropic displacement parameters, bond valence sum, bond lengths, and bond angles are listed in Tables S3−S6.

Table S1. Crystal data and structure refinement for $NaMg_4(VO_4)_3$.

Empirical formula	$NaMg_4(VO_4)_3$
Formula weight	465.027
Temperature	287.00 K
Crystal system	Trigonal
Space group	$I\bar{4}2d$
Unit cell dimensions	a= 6.8673(6) Å c=19.2548(7) Å
Volume, Z	910.83(8) $Å^3$, 4
Density (calculated)	3.391 Mg/m^3
Absorption coefficient	3.411 mm^{-1}
F(000)	901.094
Crystal size	0.14 x 0.12 x 0.1 mm^3
2θ range for data collection	3.15 to 27.48°
Index ranges	$-8 \leq h \leq 8$, $-7 \leq k \leq 8$, $-22 \leq l \leq 24$
Reflections collected	2986
Independent reflections	508 [R_{int}= 0.0536]
Completeness to theta	97.21.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	508 / 0 / 48
Goodness-of-fit on F^2	1.0060
Final R indices [$F_o^2>2\sigma(F_c^2)$] [a]	R_1= 0.0187, wR_1 = 0.0438
R indices (all data) [a]	R_1= 0.0194, wR_1 = 0.0446
Largest diff. peak and hole	0.2438 and -0.2383 e.$Å^{-3}$

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = \left[\sum w\left(F_o^2 - F_c^2\right)^2/\sum wF_o^4\right]^{1/2}$ for $F_o^2 > 2\sigma\left(F_o^2\right)$.

Table S2. Crystal data and structure refinement for $LiMg_4(VO_4)_3$.

Empirical formula	$LiMg_4(VO_4)_3$
Formula weight	449.00
Temperature	287.00 K
Crystal system	Trigonal
Space group	$I\bar{4}2d$
Unit cell dimensions	a= 6.8673(6) Å c=18.968(7) Å
Volume, Z	894.55(19) $Å^3$, 4
Density (calculated)	3.334 Mg/m^3
Absorption coefficient	3.422 mm^{-1}
F(000)	864
Crystal size	0.12 x 0.11 x 0.1 mm^3
2θ range for data collection	3.155° to 27.477°
Index ranges	-8 ≤ h ≤ 8, -8 ≤ k ≤ 8, -24 ≤ l ≤ 24
Reflections collected	2887
Independent reflections	498 [R_{int}= 0.0769]
Completeness to theta	95.2.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	498 / 0 / 47
Goodness-of-fit on F^2	1.180
Final R indices [$F_o^2>2\sigma(F_c^2)$] [a]	R_1= 0.0184, wR_1 = 0.0468
R indices (all data) [a]	R_1= 0.0187, wR_1 = 0.0470
Largest diff. peak and hole	0.255 and -0.319 e.$Å^{-3}$

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = \left[\sum w\left(F_o^2 - F_c^2\right)^2/\sum wF_o^4\right]^{1/2}$ for $F_o^2 > 2\sigma\left(F_o^2\right)$.

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $NaMg_4(VO_4)_3$. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
V(1)	5000	0	2500	6(1)
V(2)	2500	3488(1)	3750	6(1)
Mg(1)	10000	0	2742(1)	9(1)
Mg(2)	7500	2412(2)	3750	8(1)
Na(3)	5000	5000	5000	12(1)
O(3)	1988(3)	5084(3)	4410(1)	9(1)
O(2)	4575(3)	2277(3)	4015(1)	9(1)
O(1)	7066(3)	551(3)	2955(1)	10(1)

Table S4. Bond lengths [Å] and angles [°] for $NaMg_4(VO_4)_3$.

V(1)-Mg(2)	3.3915(7)	Na(3)-O(3)#5	2.364(2)
V(1)-Mg(2)#1	3.3915(7)	Na(3)-O(3)#15	2.364(2)
V(1)-Mg(2)#2	3.3915(7)	Na(3)-O(3)#6	2.364(2)
V(1)-O(1)	1.7115(19)	Na(3)-O(2)	2.681(2)
V(1)-O(1)#4	1.7115(19)	Na(3)-O(2)#15	2.681(2)
V(1)-O(1)#3	1.7115(19)	Na(3)-O(2)#5	2.681(2)
V(1)-O(1)#1	1.7115(19)	Na(3)-O(2)#6	2.681(2)
V(2)-Mg(2)#5	2.8199(16)	Mg(2)-O(2)	2.0776(18)
V(2)-Na(3)#2	3.1355(2)	Mg(2)-O(1)#11	2.018(2)
V(2)-Na(3)#6	3.1355(2)		
V(2)-O(3)	1.715(2)	O(1)#3-V(1)-O(1)	118.48(13)
V(2)-O(3)#7	1.715(2)	O(1)#4-V(1)-O(1)#1	118.48(13)
V(2)-O(2)#7	1.7291(18)	O(1)#4-V(1)-O(1)#3	105.16(6)
V(2)-O(2)	1.7291(18)	O(1)#1-V(1)-O(1)	105.16(6)
Mg(1)-Mg(2)	3.0782(11)	O(1)#1-V(1)-O(1)#3	105.16(6)
Mg(1)-Mg(2)#8	3.0782(11)	O(1)#4-V(1)-O(1)	105.16(6)
Mg(1)-O(3)#9	2.108(2)	O(3)#7-V(2)-O(3)	100.42(13)
Mg(1)-O(3)#10	2.108(2)	O(3)#7-V(2)-O(3)	100.42(13)
Mg(1)-O(2)#11	2.141(2)	O(2)#7-V(2)-O(3)#7	105.02(9)
Mg(1)-O(2)#12	2.141(2)	O(2)-V(2)-O(3)#7	110.92(9)
Mg(1)-O(1)#8	2.093(2)	O(2)#7-V(2)-O(3)	110.92(9)
Mg(1)-O(1)	2.093(2)	O(2)-V(2)-O(3)	105.02(9)
Mg(2)-Na(3)#6	3.4521(7)	O(2)-V(2)-O(2)#7	122.44(13)
Mg(2)-Na(3)#13	3.4521(7)	O(2)#12-Mg(1)-O(3)#10	170.52(9)
Mg(2)-O(3)#5	2.169(2)	O(2)#11-Mg(1)-O(3)#9	170.52(9)
Mg(2)-O(3)#14	2.169(2)	O(2)#12-Mg(1)-O(3)#9	91.71(7)
Mg(2)-O(2)#11	2.0776(18)	O(2)#11-Mg(1)-O(3)#10	91.71(7)
Mg(2)-O(1)	2.018(2)	O(2)#11-Mg(1)-O(2)#12	96.16(12)
Na(3)-O(3)	2.364(2)	O(1)#8-Mg(1)-O(3)#10	103.87(8)

O(1)#8-Mg(1)-O(3)#9	93.30(8)	O(3)#15-Na(3)-O(3)#6	122.51(9)
O(1)-Mg(1)-O(3)#9	103.87(8)	O(3)#5-Na(3)-O(3)	122.51(9)
O(1)-Mg(1)-O(3)#10	93.30(8)	O(3)#5-Na(3)-O(3)#6	103.37(4)
O(1)-Mg(1)-O(2)#11	82.46(7)	O(2)#15-Na(3)-O(3)	162.73(6)
O(1)#8-Mg(1)-O(2)#11	82.54(8)	O(2)#6-Na(3)-O(3)#15	74.84(6)
O(1)-Mg(1)-O(2)#12	82.54(8)	O(2)#5-Na(3)-O(3)	74.84(6)
O(1)#8-Mg(1)-O(2)#12	82.46(7)	O(2)#15-Na(3)-O(3)#15	65.25(6)
O(1)#8-Mg(1)-O(1)	157.46(12)	O(2)#5-Na(3)-O(3)#15	162.73(6)
O(2)-Mg(2)-O(3)#14	91.26(8)	O(2)#15-Na(3)-O(3)#5	74.06(6)
O(2)-Mg(2)-O(3)#5	92.81(8)	O(2)#6-Na(3)-O(3)	74.06(6)
O(2)#11-Mg(2)-O(3)#14	92.81(8)	O(2)-Na(3)-O(3)	65.25(6)
O(2)#11-Mg(2)-O(3)#5	91.26(8)	O(2)#6-Na(3)-O(3)#6	65.25(6)
O(2)#11-Mg(2)-O(2)	174.87(13)	O(2)#5-Na(3)-O(3)#5	65.25(6)
O(1)-Mg(2)-O(3)#14	92.03(8)	O(2)#5-Na(3)-O(3)#6	74.06(6)
O(1)-Mg(2)-O(3)#5	166.45(9)	O(2)-Na(3)-O(3)#15	74.06(6)
O(1)#11-Mg(2)-O(3)#14	166.45(9)	O(2)-Na(3)-O(3)#6	162.73(6)
O(1)#11-Mg(2)-O(3)#5	92.03(8)	O(2)-Na(3)-O(3)#5	74.84(6)
O(1)#11-Mg(2)-O(2)	85.90(8)	O(2)#15-Na(3)-O(3)#6	74.84(6)
O(1)-Mg(2)-O(2)#11	85.90(8)	O(2)#6-Na(3)-O(3)#5	162.73(6)
O(1)-Mg(2)-O(2)	90.85(8)	O(2)#6-Na(3)-O(2)	120.02(5)
O(1)#11-Mg(2)-O(2)#11	90.85(8)	O(2)#5-Na(3)-O(2)#15	120.02(5)
O(1)#11-Mg(2)-O(1)	101.25(13)	O(2)#5-Na(3)-O(2)	89.96(8)
O(3)-Na(3)-O(3)#6	103.37(4)	O(2)#15-Na(3)-O(2)	120.02(5)
O(3)#15-Na(3)-O(3)	103.37(4)	O(2)#15-Na(3)-O(2)#6	89.96(8)
O(3)#5-Na(3)-O(3)#15	103.37(4)	O(2)#5-Na(3)-O(2)#6	120.02(5)

Symmetry transformations used to generate equivalent atoms:

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

#5 -y+1,x+1,-z #6 x,y+1,z+1 #7 3 #8 -y+2,x,-z

#9+5 #10 x+1/2,-y,-z-1/4 #11+4 #12 y,-x,-z

#13+5 #14 y,-x+1,-z #15+3 #16 8 #17 y-1,-x,-z

#18 y-1/2,x,z-1/4 #19 8 #20 y-1,-x+1,-z #21 y-1/2,x-1,z-1/4

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $LiMg_4(VO_4)_3$ U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
V(1)	5000	0	2500	6(1)
V(2)	2500	3502(1)	3750	6(1)
Mg(2)	10000	0	2744(1)	9(1)
Mg(1)	7500	2412(2)	3750	8(1)
O(3)	2094(4)	5092(4)	4434(1)	10(1)
O(2)	4572(3)	2275(4)	3988(1)	10(1)
O(1)	7084(4)	534(4)	2955(1)	9(1)
Li(1)	5000	5000	5000	13(3)

Table S6. Bond lengths [Å] and angles [°] for $LiMg_4(VO_4)_3$.

V(2)-Mg(1)#1	3.3665(9)	O(3)#3-V(2)-O(3)#2	104.73(8)
V(2)-Mg(1)	3.3665(9)	O(3)#2-V(2)-O(3)#1	104.73(8)
V(2)-Mg(1)#2	3.3665(9)	O(3)#2-V(2)-O(3)	119.43(17)
V(2)-Mg(1)#3	3.3665(9)	O(3)#1-V(2)-O(3)	104.73(8)
V(2)-O(3)#3	1.711(3)	O(3)#3-V(2)-O(3)#1	119.43(17)
V(2)-O(3)#1	1.711(3)	O(3)#3-V(2)-O(3)	104.73(8)
V(2)-O(3)	1.711(3)	O(3)#3-V(2)-O(3)#2	104.73(8)
V(2)-O(3)#2	1.711(3)	O(3)#2-V(2)-O(3)#1	104.73(8)
V(1)-Mg(1)#4	2.800(2)	O(1)-V(1)-O(1)#5	101.14(18)
V(1)-O(1)#5	1.719(3)	O(2)-V(1)-O(1)	104.36(13)
V(1)-O(1)	1.719(3)	O(2)-V(1)-O(1)#5	112.12(12)
V(1)-O(2)#5	1.714(2)	O(2)#5-V(1)-O(1)	112.12(12)
V(1)-O(2)	1.715(2)	O(2)#5-V(1)-O(1)#5	104.36(13)
V(1)-Li(1)	3.1028(4)	O(2)#5-V(1)-O(2)	121.10(18)
V(1)-Li(1)#5	3.1028(4)	O(1)#8-Mg(2)-O(1)#7	86.25(15)
Mg(2)-Mg(1)	3.0577(15)	O(1)#7-Mg(2)-O(2)#10	89.64(10)
Mg(2)-Mg(1)#6	3.0577(15)	O(1)#8-Mg(2)-O(2)#10	172.74(10)
Mg(2)-O(1)#7	2.105(3)	O(1)#8-Mg(2)-O(2)#9	89.64(10)
Mg(2)-O(1)#8	2.105(3)	O(1)#7-Mg(2)-O(2)#9	172.74(10)
Mg(2)-O(2)#9	2.155(3)	O(2)#10-Mg(2)-O(2)#9	95.04(16)
Mg(2)-O(2)#10	2.155(3)	O(3)-Mg(2)-O(1)#8	103.43(10)
Mg(2)-O(3)#6	2.074(3)	O(3)#6-Mg(2)-O(1)#8	92.80(10)
Mg(2)-O(3)	2.074(3)	O(3)-Mg(2)-O(1)#7	92.80(10)
Mg(2)-Li(1)#11	3.4648(4)	O(3)#6-Mg(2)-O(1)#7	103.42(11)
Mg(2)-Li(1)#10	3.4648(4)	O(3)#6-Mg(2)-O(2)#9	82.73(10)
Mg(1)-O(1)#12	2.163(3)	O(3)-Mg(2)-O(2)#9	82.33(10)
Mg(1)-O(1)#4	2.163(3)	O(3)#6-Mg(2)-O(2)#10	82.33(10)
Mg(1)-O(2)#10	2.063(2)	O(3)-Mg(2)-O(2)#10	82.73(10)
Mg(1)-O(2)	2.063(2)	O(3)#6-Mg(2)-O(3)	157.80(16)
Mg(1)-O(3)#10	2.009(3)	O(1)#4-Mg(1)-O(1)#12	75.73(15)
Mg(1)-O(3)	2.009(3)	O(2)-Mg(1)-O(1)#4	91.87(11)
Mg(1)-Li(1)	3.4215(9)	O(2)-Mg(1)-O(1)#12	92.53(10)
O(1)-Li(1)	2.267(3)	O(2)#10-Mg(1)-O(1)#4	92.53(11)
O(3)#2-V(2)-O(3)	119.43(17)	O(2)#10-Mg(1)-O(1)#12	91.87(11)
O(3)#1-V(2)-O(3)	104.73(8)	O(2)-Mg(1)-O(2)#10	174.43(18)
O(3)#3-V(2)-O(3)#1	119.43(17)	O(3)#10-Mg(1)-O(1)#12	168.00(12)
O(3)#3-V(2)-O(3)	104.73(8)	O(3)-Mg(1)-O(1)#4	168.00(12)

O(3)#10-Mg(1)-O(1)#4	92.32(10)	O(1)#4-Li(1)-O(1)	123.51(13)
O(3)-Mg(1)-O(1)#12	92.32(10)	O(1)#14-Li(1)-O(1)	102.94(5)
O(3)#10-Mg(1)-O(2)	86.71(11)	O(1)#14-Li(1)-O(1)#4	102.94(6)
O(3)#10-Mg(1)-O(2)#10	89.69(11)	O(1)#14-Li(1)-O(1)#15	123.51(13)
O(3)-Mg(1)-O(2)	89.69(11)	O(1)#15-Li(1)-O(1)#4	102.94(5)
O(3)-Mg(1)-O(2)#10	86.71(11)	O(1)#15-Li(1)-O(1)	102.94(6)
O(3)-Mg(1)-O(3)#10	99.65(17)	O(1)#4-Li(1)-O(1)	123.51(13)
O(1)#14-Li(1)-O(1)#15	123.51(13)	O(1)#14-Li(1)-O(1)	102.94(5)
O(1)#15-Li(1)-O(1)#4	102.94(5)	O(1)#14-Li(1)-O(1)#4	102.94(6)
O(1)#15-Li(1)-O(1)	102.94(6)		

Symmetry transformations used to generate equivalent atoms:

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

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

#7 y+1/2,x,z-1/4 #8 -y+3/2,-x,z-1/4 #9 x+1/2,-y,-z+3/4

#10 -x+3/2,y,-z+3/4 #11 -x+3/2,y-1,-z+3/4 #12 x+1/2,-y+1,-z+3/4

#13 -y+0,-x+3/2,z+1/4 #14 y,-x+1,-z+1 #15 -y+1,x,-z+1

Table S7. Basic information on vanadates containing the [VO_4] quaternary alkali metal.

No.	Compound	Space group (Number)	NCS/CS	Ref.
1	$K(LiVO_4)$	*C*2/*m* (12)	CS	3
2	$Rb_2(LiVO_4)$	*Cmc*2_1 (36)	NCS	4
3	$Cs_2(LiVO_4)$	*Cmc*2_1 (36)	NCS	4
4	$Cs_2Na(VO_4)$	*P*2_1/*m* (11)	CS	5
5	$LiNiVO_4$	*Imma* (74)	CS	6
6	$LiNiVO_4$	$Fd\bar{3}m$ (227)	CS	6
7	$LiNiVO_4$	*P*$4_1$22 (91)	CS	6
8	$LiNiVO_4$	*Imma* (74)	CS	6
9	$LiCoVO_4$	$Fd\bar{3}m$ (227)	NCS	6
10	$LiCoVO_4$	*P*$4_1$22 (91)	NCS	6
11	$LiMn(VO_4)$	$Fd\bar{3}m$ (227)	CS	7
12	$LiMn(VO_4)$	*Cmcm* (63)	CS	7
13	$LiCuVO_4$	*Imma* (74)	CS	8
14	$LiZn(VO_4)$	$R\bar{3}$ (148)	CS	9
15	$Li\ La_2O_2(VO_4)$	$P\bar{1}$ (2)	CS	9
16	$LiNd_5O_5(VO_4)_2$	*C*2/*m* (12)	CS	10
17	$Na_3Er(VO_4)_2$	*P*2_1/*c* (14)	CS	11
18	$Na_3La(VO_4)_2$	*Pca*2_1 (29)	NCS	12
19	$NaPb_4(VO_4)_3$	*P*6_3/*mmc* (194)	CS	13
20	$NaMn_4(VO_4)_3$	$I\bar{4}2d$ (122)	NCS	13
21	$Na_2Mn_3(VO_4)_3$	*C*2/*c* (15)	CS	14
22	$NaCd(VO_4)$	*Cmcm* (63)	CS	15
23	$Na_3Nd\ (VO_4)_2$	*Cc* (9)	NCS	16
24	$NaSrVO_4$	*P*2_1/*c* (14)	CS	17
25	$NaSrVO_4$	*P*6_3*mc* (186)	NCS	17

26	$MnNa(VO_4)$	*Pnma* (62)	CS	18
27	$Na_3Sc_2(VO_4)_3$	$Ia\bar{3}d$ (230)	CS	14
28	$Cd_4K(VO_4)_3$	*Cc* (9)	NCS	19
29	$KTh_2(VO_4)_3$	*C*2/*c* (15)	CS	20
30	$K_3Er(VO_4)_2$	*C*2/*c* (15)	CS	21
31	$KPb_4(VO_4)_3$	$P6_3/m$ (176)	CS	13
32	$K_2(UO_2)_2(VO_4)_2$	$P2_1$/c (14)	CS	22
33	$KCd(VO_4)$	$P2_1$/c (14)	CS	23
34	$KSr(VO_4)$	$p2_12_12_1$ (19)	CS	24
35	$K_3Eu(VO_4)_2$	$P2_1/m$ (11)	CS	25
36	KMn(VO4)	$P2_1$/c (14)	CS	26
37	$K_3Bi_2(VO_4)_3$	*C*2/*c* (15)	CS	27
38	$K_3Y(VO_4)_2$	$P\bar{3}m1$ (164)	CS	28
39	$K_3Sc(VO_4)_2$	$P\bar{3}m1$ (164)	CS	28
40	$K_3Dy(VO_4)_2$	$P\bar{3}m1$ (164)	CS	28
41	$K_3Yb(VO_4)_2$	$P\bar{3}m1$ (164)	CS	28
42	$K_3Er(VO_4)_2$	$P\bar{3}m1$ (164)	CS	28
43	$K_3Ho(VO_4)_2$	$P\bar{3}m1$ (164)	CS	28
44	$K_3Lu(VO_4)_2$	$P\bar{3}m1$ (164)	CS	29
45	$K_3Tm(VO_4)_2$	$P\bar{3}m1$ (164)	CS	29
46	$Cs_{11}(Ge_9)_2(VO_4)$	$P2_1$/c (14)	CS	29

* NCS: non-centrosymmetric. CS: centrosymmetric.

Table S8. Basic information on vanadates containing the [VO_4] quaternary alkaline earth metal.

No.	Compound	Space group (Number)	NCS/CS*	Ref.
1	$BaMg_2(VO_4)_2$	$I4_1/acd$ (142)	CS	30
2	$Ba_2Sr(VO_4)_2$	$R\bar{3}$ (148)	NCS	31
3	$BaSr_2(VO_4)_2$	$R\bar{3}$ (148)	NCS	32
4	$Ni_2Mg(VO_4)_2$	*Cmca* (64)	CS	32
5	$NiMg_2(VO_4)_2$	*Cmca* (64)	CS	32
6	$Mg_2Co(VO_4)_2$	*Cmca* (64)	CS	31
7	$CuMgVO_4$	*Cmca* (64)	CS	33
8	$AgMaVO_4$	*Pnma* (62)	CS	33
9	$Ca_9Tb(VO_4)_7$	*R*3*c* (161)	NCS	33
10	$Ca_9Dy(VO_4)_7$	*R*3*c* (161)	NCS	34
11	$Ca_9Ho(VO_4)_7$	*R*3*c* (161)	NCS	34
12	$Ca_9Nd(VO_4)_7$	*R*3*c* (161)	NCS	35
13	$Ca_9Sm(VO_4)_7$	*R*3*c* (161)	NCS	35
14	$Ca_9Gd(VO_4)_7$	*R*3*c* (161)	NCS	35
15	$Ca_9Er(VO_4)_7$	*R*3*c* (161)	NCS	36
16	$Ca_9Tm(VO_4)_7$	*R*3*c* (161)	NCS	36
17	$Ca_9Yb(VO_4)_7$	*R*3*c* (161)	NCS	36
18	$Ca_9Lu(VO_4)_7$	*R*3*c* (161)	NCS	36
19	$BiCa_9(VO_4)_7$	$R\bar{3}$ (148)	CS	37
20	$Ca_9La(VO_4)_7$	*R*3*c* (161)	NCS	38
21	$Ca_9Pr(VO_4)_7$	*R*3*c* (161)	NCS	38
22	$Ca_2Pb(VO_4)_2$	*R*3*c* (161)	NCS	39
23	$Ca_9Y(VO_4)_7$	*R*3*c* (161)	NCS	40
24	$AgCaVO_4$	*Pnma* (62)	CS	41
25	$Sr_9In(VO_4)_7$	*R*3*c* (161)	NCS	42

26	$CeSr(VO_4)$	*I*4/*mmm* (139)	CS	43
27	$PrSr(VO_4)$	*I*4/*mmm* (139)	CS	43
28	$NSr(VO_4)$	*I*4/*mmm* (139)	CS	43
29	$Sr_9Tm\ (VO_4)_7$	*R*3*c* (161)	NCS	44
30	$Sr_9Yb(VO_4)_7$	*R*3*c* (161)	CS	44
31	$Sr_9Lu(VO_4)_7$	*R*3*c* (161)	CS	44
32	$SrCo(VO_4)_2$	$I4_1cd$ (110)	NCS	45
33	$SrMn_2(VO_4)_2$	$I4_1cd$ (110)	NCS	45
34	$SrNi_2(VO_4)_2$	$I4_1cd$ (110)	NCS	46
35	$(Sr\ La)VO_4$	*I*4/*mmm* (139)	CS	47
36	$LaSrVO_4$	*I*4/*mmm* (139)	CS	43
37	$BaCo_2(VO_4)_2$	$I4_1/acd$ (142)	CS	48
38	$BaTi(VO_4)$	*Pnma* (62)	CS	49
39	$BaMn_2(VO_4)_2$	$I4_1/acd$ (142)	CS	50

* NCS: non-centrosymmetric. CS: centrosymmetric.

Table S9. Basic information on vanadates containing the [VO_4] quaternary alkali and alkaline earth metal.

No.	Compound	Space group (Number)	NCS/CS*	Ref.
1	$LiMg(VO_4)$	*Cmcm* (63)	CS	51
2	$LiMg_4(VO_4)_3$	$I\bar{4}2d$ (122)	NCS	52
3	$NaMg_4(VO_4)_3$	$I\bar{4}2d$ (122)	NCS	53
4	$NaCaVO_4$	*Cmcm* (63)	CS	54
5	$NaSrVO_4$	$p2_12_12_1$ (19)	CS	55
6	$KBa(VO_4)$	*Pnma* (62)	CS	56
7	$RbSr(VO_4)$	*Pnma* (62)	CS	57

* NCS: non-centrosymmetric. CS: centrosymmetric.

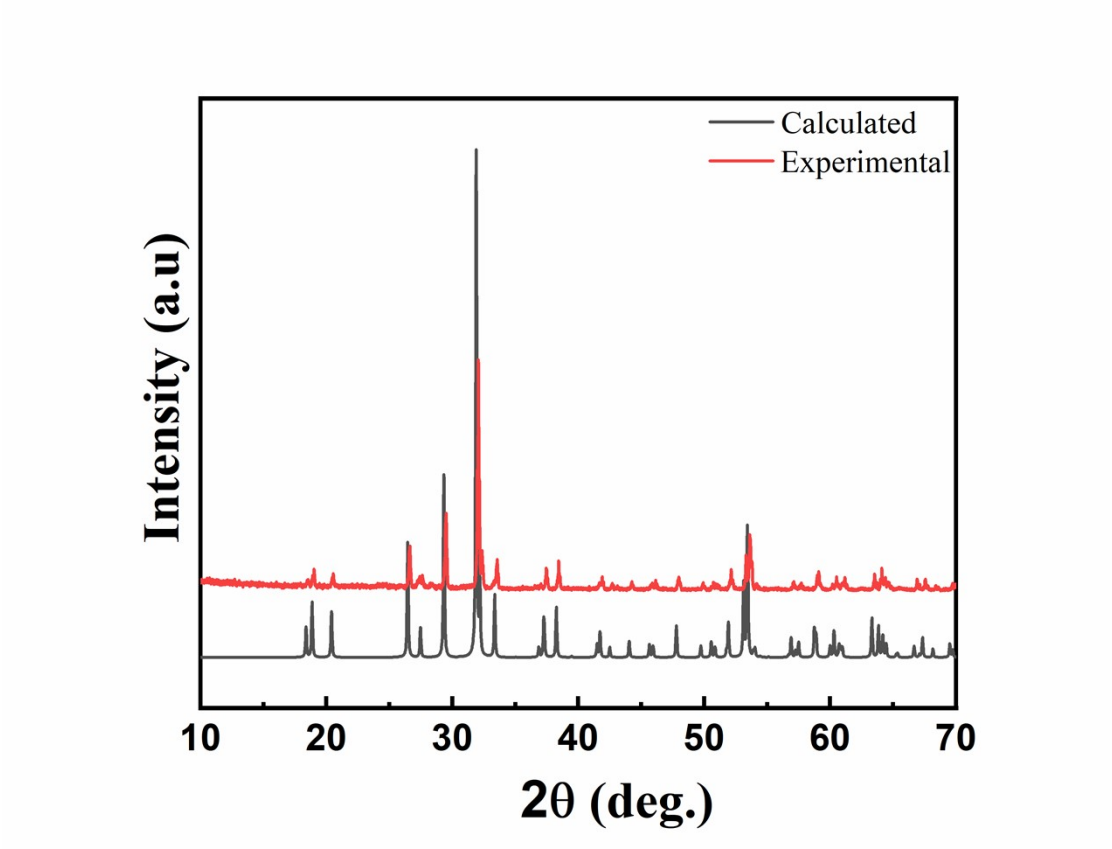

Figure S1. Powder XRD patterns at 850 °C for $NaMg_4(VO_4)_3$.

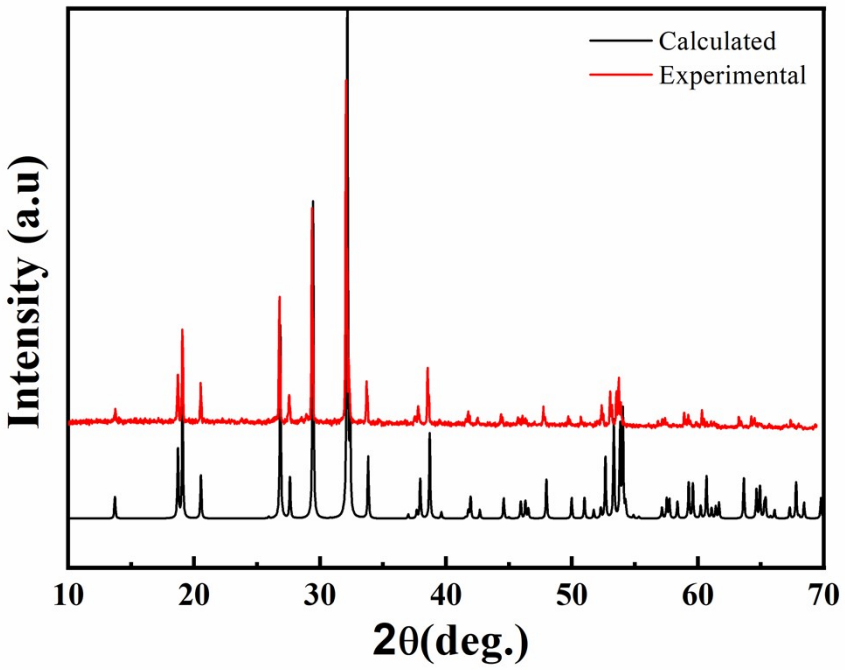

Figure S2. Powder XRD patterns at 800 °C for $LiMg_4(VO_4)_3$.

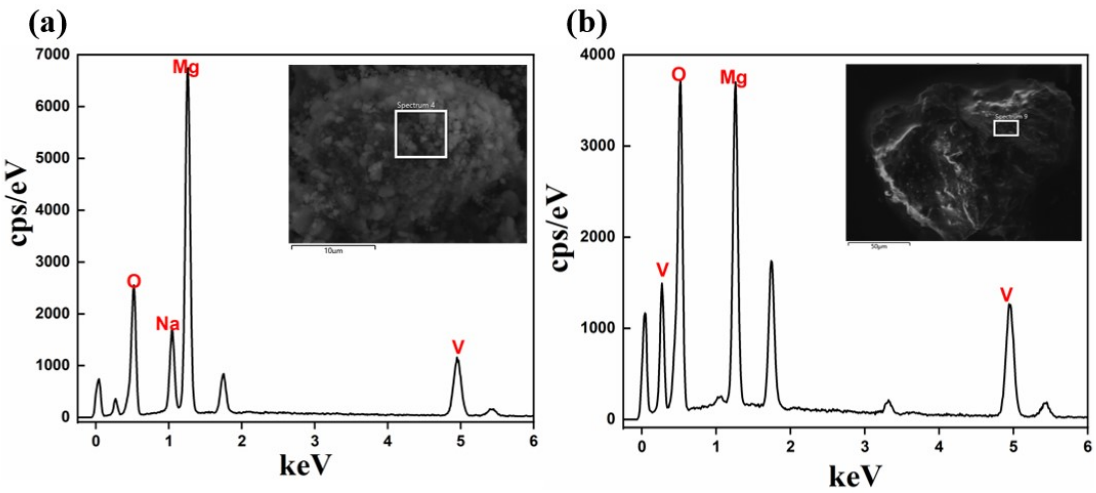

Figure S3. EDS spectrum of (a) $NaMg_4(VO_4)_3$ and (b) $LiMg_4(VO_4)_3$.

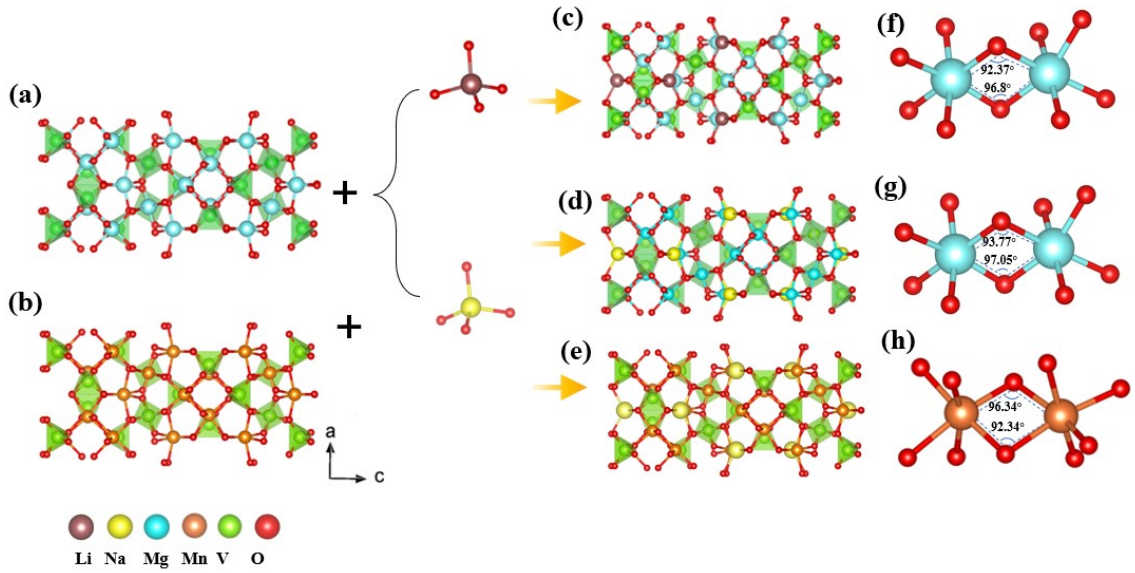

Figure S4. (a) Three-dimensional network of edge-sharing MgO_6 octahedra associated with VO_4 groups; (b) Three-dimensional network of edge-sharing MnO_6 octahedra associated with VO_4 groups; (c) The crystal structure of $LiMg_4(VO_4)_3$; (d) The crystal structure of $NaMg_4(VO_4)_3$; (e) The crystal structure of $NaMn_4(VO_4)_3$; (f) The Mg-O-Mg bond Angle is 92.37° and 96.8° in the $LiMg_4(VO_4)_3$; (g) The Mg-O-Mg bond Angle is 93.77 ° and 97.05° in $NaMg_4(VO_4)_3$; (h) The Mg-O-Mg bond Angle is 96. 34° and 92.34° in $NaMn_4(VO_4)_3$;
(Li brown; Na yellow; Mg blue; Mn orange; V green; O red;)

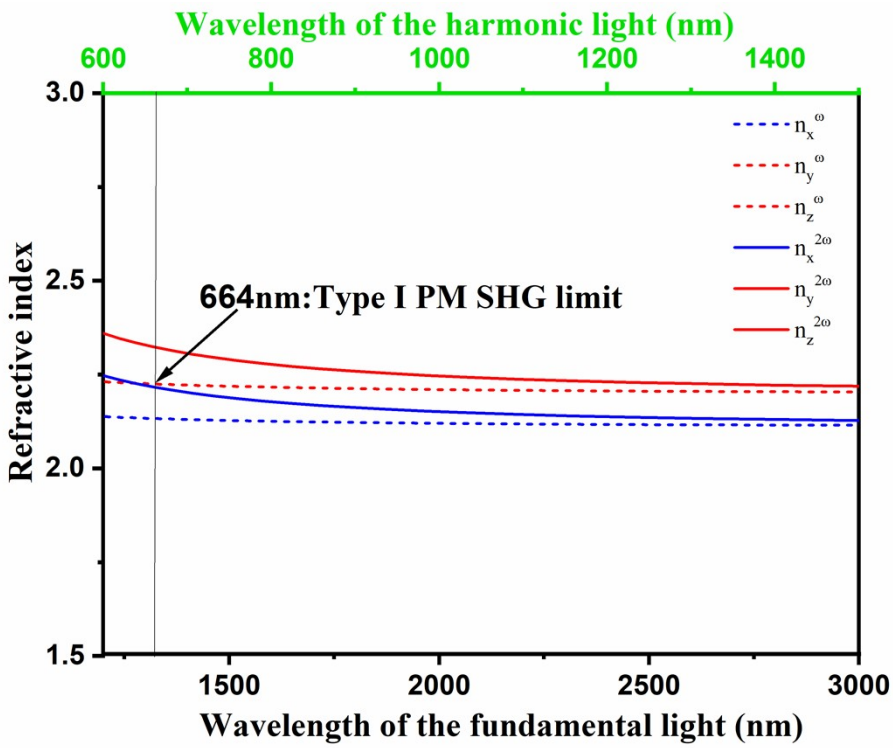

Figure S5. Calculated refractive index dispersion curves of $NaMg_4(VO_4)_3$.

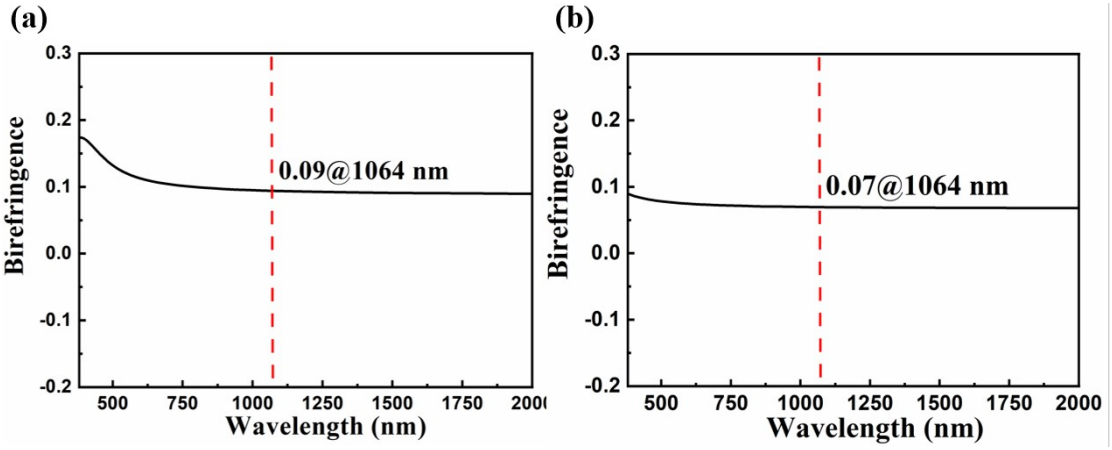

Figure S6. Birefringence curves of (a) $NaMg_4(VO_4)_3$ and (b) $LiMg_4(VO_4)_3$.

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