Supporting Information:

Periodic Tendril Perversion and Helices in the $AMoO_2F_3$ (A = K, Rb, NH_4, Tl) Family

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Table S1 Crystallographic data for $(Rb/Tl/NH_4)MoO_2F_3$

Compound	$RbMoO_2F_3$	$TlMoO_2F_3$	$NH_4MoO_2F_3$
Formula weight	270.41	389.31	198.95
Temperature (K)	100.04	99.96	200.01
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a (Å)	8.4691(6)	8.3492(3)	8.47740(10)
b (Å)	13.3818(9)	13.4494(5)	13.39660(10)
c (Å)	28.188(2)	28.2717(10)	28.4385(3)
α (°)	90	90	90
β (°)	95.692(4)	95.004(2)	95.0730(10)
γ (°)	90	90	90
Volume ($Å^3$)	3178.8(4)	3162.6(2)	3217.06(6)
Z	28	28	28
Density (g/cm^3)	3.955	5.723	2.875
μ (mm^{-1})	13.494	38.353	2.819
F(000)	3416.0	4648.0	2576.0
Crystal size (mm^3)	0.167 × 0.123 × 0.097	0.325 × 0.232 × 0.195	0.278 × 0.262 × 0.154
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for collection (°)	2.904 to 59.41	2.892 to 72.908	5.702 to 76.458
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 18, -39 ≤ l ≤ 39	-13 ≤ h ≤ 13, -22 ≤ k ≤ 17, -38 ≤ l ≤ 47	-14 ≤ h ≤ 14, -22 ≤ k ≤ 22, -47 ≤ l ≤ 48
Reflections collected	72095	21199	46287
Independent reflections	4492 [R_{int} = 0.0700, R_{sigma} = 0.0259]	7701 [R_{int} = 0.0770, R_{sigma} = 0.0940]	8446 [R_{int} = 0.0280, R_{sigma} = 0.0180]
Data/restraints/parameters	4492/0/225	7701/0/225	8446/0/225
Goodness-of-fit on F^2	1.225	1.018	1.116
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0260, wR_2 = 0.0600	R_1 = 0.0560, wR_2 = 0.1310	R_1 = 0.0207, wR_2 = 0.0502
Final *R* indexes [all data]	R_1 = 0.0266, wR_2 = 0.0603	R_1 = 0.0660, wR_2 = 0.1369	R_1 = 0.0227, wR_2 = 0.0510
Largest diff. peak and hole (e^-/A^3)	1.63/-1.03	7.76/-5.14	1.07/-0.85

Table S2 Crystallographic data for both $KMoO_2F_3$ enantiomorphs

Compound	Δ-$KMoO_2F_3$	Λ-$KMoO_2F_3$
Formula weight	224.04	224.04
Temperature (K)	100.02	100.01
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	11.3563(5)	11.37930(10)
b (Å)	11.8657(5)	11.8884(2)
c (Å)	12.7391(6)	12.7447(2)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å^3)	1716.60(13)	1724.12(4)
Z	16	16
Density (g/cm^3)	3.468	3.452
μ (mm^{-1})	3.979	3.962
F(000)	1664.0	1664.0
Crystal size (mm^3)	0.182 × 0.097 × 0.094	0.344 × 0.194 × 0.158
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for collection (°)	4.692 to 61.146	4.686 to 76.054
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -18 ≤ l ≤ 16	-18 ≤ h ≤ 18, -12 ≤ k ≤ 19, -19 ≤ l ≤ 21
Reflections collected	21427	24568
Independent reflections	5241 [R_{int} = 0.0225, R_{sigma} = 0.0187]	8805 [R_{int} = 0.0297, R_{sigma} = 0.0343]
Data/restraints/parameters	5241/0/253	8805/0/254
Goodness-of-fit on F^2	1.192	1.045
Final *R* indexes [$I \geq 2\sigma$ (*I*)]	R_1 = 0.0129, wR_2 = 0.0314	R_1 = 0.0220, wR_2 = 0.0457
Final *R* indexes [all data]	R_1 = 0.0130, wR_2 = 0.0314	R_1 = 0.0235, wR_2 = 0.0463
Largest diff. peak and hole (e$^-$/A^3)	0.44/-0.73	0.78/-1.02
Flack parameter	-0.004(10)	-0.003(15)

Table S3 Cs-F and Cs-O distances shorter than the closest cation distance and individual bond valences for reported $CsMoO_2F_3$. Data from ICSD collection code 1710.

Anion	Distance (Å)	Bond Valence
O1	3.0848(471)	0.165
O1	3.0848(471)	0.165
F2	3.1007(349)	0.125
F2	3.1007(349)	0.125
F2	3.1007(349)	0.125
F2	3.1007(349)	0.125
F2	3.2464(508)	0.084
F2	3.2464(508)	0.084
O1	3.6566(260)	0.035
O1	3.6556(260)	0.035
O1	3.6556(260)	0.035
O1	3.6556(260)	0.035
F1	3.8914(250)	0.019
F1	3.8914(25)	0.019
F1	3.8914(25)	0.019
F1	3.8914(25)	0.019

Table S4 Rb-F and Rb-O distances shorter than the closest cation distance and individual bond valences in $RbMoO_2F_3$.

Rb1			Rb2			Rb3			Rb4		
Anion	Distance (Å)	Bond Valence	Anion	Distance (Å)	Bond Valence	Anion	Distance (Å)	Bond Valence	Anion	Distance (Å)	Bond Valence
F6	2.7556(29)	0.200	O2	2.8421(30)	0.209	F11	2.8103(29)	0.172	F9	2.8170(23)	0.169
F2	2.8449(52)	0.157	O5	2.8534(39)	0.203	F11	2.8103(29)	0.172	F11	2.8177(22)	0.169
F8	2.8511(45)	0.154	F8	2.8576(23)	0.152	F9	2.8410(27)	0.159	F7	2.9630(31)	0.114
O1	2.8811(30)	0.188	F5	2.8947(52)	0.137	F9	2.8410(27)	0.159	F2	3.0159(42)	0.0989
F3	2.9155(26)	0.130	O7	2.9867(28)	0.141	O6	3.0094(30)	0.133	F10	3.0504(33)	0.0901
F6	2.9904(31)	0.106	O1	3.0838(51)	0.109	O6	3.0094(30)	0.133	F5	3.1146(23)	0.0758
O3	2.9915(32)	0.140	F4	3.0850(31)	0.0821	F5	3.0412(45)	0.0924	O6	3.1635(35)	0.0877
F3	3.0756(39)	0.0842	F2	3.1002(25)	0.0788	F5	3.0412(45)	0.0924	O4	3.1707(29)	0.0860
O3	3.1096(49)	0.0101	F3	3.1857(44)	0.0625	O4	3.3072(59)	0.0595	O2	3.2138(54)	0.0766
O5	3.5701(28)	0.0292	F1	3.4759(43)	0.0285	O4	3.3072(59)	0.0595	F4	3.2297(47)	0.0555
O1	3.6007(40)	0.0269	O3	3.5244(41)	0.0331	F7	3.4714(29)	0.0289	O7	3.3059(31)	0.0597
F1	3.6076(29)	0.0200	F6	3.6419(38)	0.0182	F7	3.4714(29)	0.0289	O5	3.4271(40)	0.0430
F4	3.7505(68)	0.0136	O4	3.7131(52)	0.0199	---	---	---	O6	3.7723(56)	0.0169
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Table S5 K-F and K-O distances shorter than the closest cation distance and individual bond valences.

K1			K2			K3			K4		
Anion	Distance (Å)	Bond Valence	Anion	Distance (Å)	Bond Valence	Anion	Distance (Å)	Bond Valence	Anion	Distance (Å)	Bond Valence
F3	2.6162(17)	0.185	F5	2.6802(18)	0.156	F3	2.6767(17)	0.157	F8	2.6461(18)	0.171
F5	2.6333(18)	0.177	O3	2.6856(21)	0.224	F8	2.7203(17)	0.140	F6	2.6920(18)	0.151
F12	2.6963(16)	0.149	F9	2.7011(17)	0.147	F9	2.7890(17)	0.116	O1	2.7789(20)	0.174
O8	2.7685(20)	0.179	F6	2.7419(17)	0.132	F7	2.8088(17)	0.110	F4	2.8386(16)	0.101
O2	2.7846(21)	0.171	O5	2.8403(21)	0.147	F11	2.8339(17)	0.103	F1	2.8705(18)	0.093
F2	2.8554(17)	0.097	F2	2.8890(17)	0.089	O6	2.8512(21)	0.143	F12	2.9319(18)	0.079
F11	2.9253(17)	0.080	F10	2.9458(17)	0.076	O4	2.8633(20)	0.139	F11	2.9358(18)	0.078
O5	2.9583(21)	0.107	F12	2.9792(18)	0.069	F4	3.0368(16)	0.059	O7	2.9671(21)	0.105
O1	3.4327(20)	0.030	O7	3.4249(21)	0.030	O2	3.0570(21)	0.082	O8	3.1720(20)	0.060
O3	3.6170(21)	0.018	F7	3.5567(17)	0.015	O1	3.0768(20)	0.078	O4	3.4585(21)	0.028
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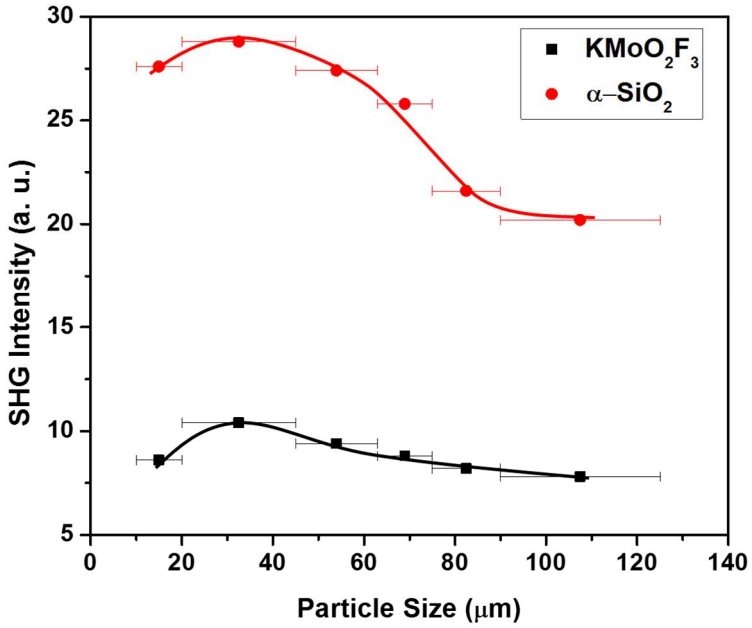

Figure S1 SHG measurements of ground $KMoO_2F_3$ crystals (blacksquare) and α-SiO_2 (red circle) as the reference with the laser at 1064 nm wavelength.

S1 Stability in Air

The relative air stability of the $AMoO_2F_3$ compounds is as follows: $NH_4MoO_2F_3$ < $KMoO_2F_3$ < (Cs/Rb/Tl)MoO_2F_3. All $AMoO_2F_3$ crystals are initially colorless and transparent. $NH_4MoO_2F_3$ decomposition is apparent within a few days, forming a yellow-green powder within two weeks $KMoO_2F_3$ is more stable, but crystals become cloudy and lose their transparency over the course of months. $AMoO_2F_3$ with A = Cs, Rb, Tl are much more stable, and their crystals did not show evidence of decomposition over the course of a year.

S2 Experimental information for SHG measurements

$KMoO_2F_3$ polycrystalline powder was ground and sieved into distinct particle size ranges (<20, 20-45, 45-63, 63-75, 75-90, 90-125 μm). Relevant comparisons with known SHG materials were made by grinding and sieving crystalline α-SiO_2 into the same particle size ranges. SHG intensity was recorded regarding to different particle range under the radiation of a laser with fundamental wavelength 1064 nm. No index matching fluid was used in any of the experiments.