Supporting Information

Synthesis, structures, properties of two magnesium silicate fluorides $Mg_5(SiO_4)_2F_2$ and $Mg_3SiO_4F_2$

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Figure S1. EDX spectra of $Mg_5(SiO_4)_2F_2$ (a) and $Mg_3SiO_4F_2$ (b).

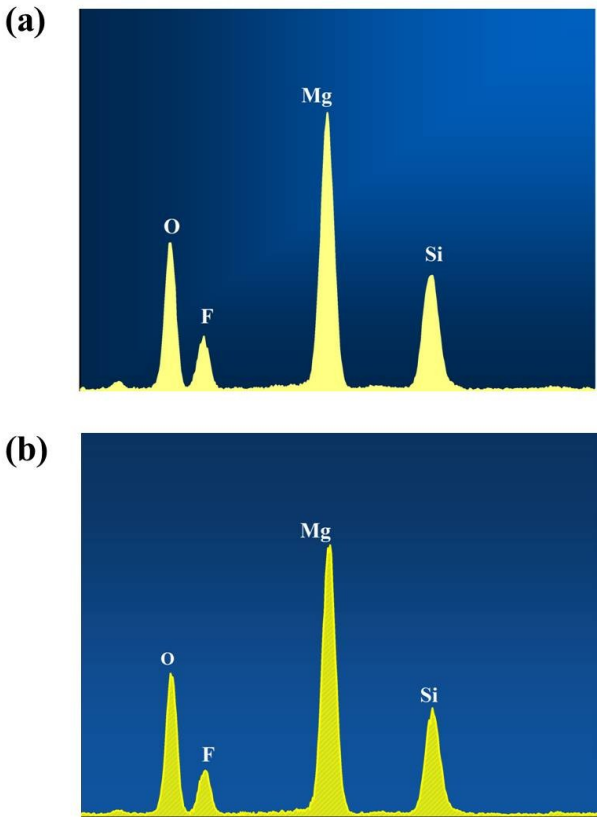

Table S1. Average EDX data for $Mg_5(SiO_4)_2F_2$ (a) and $Mg_3SiO_4F_2$ (b).

(a) Compound $Mg_5(SiO_4)_2F_2$:

Element	Weight %	Atomic %	Formula
Mg	35.52	29.67	5.07
Si	17.08	12.35	2.11
O	36.53	46.36	7.92
F	10.87	11.62	1.99

(b) Compound $Mg_3SiO_4F_2$:

Element	Weight %	Atomic %	Formula
Mg	34.86	29.05	2.96
Si	14.09	10.16	1.04
O	31.93	40.41	4.12
F	19.12	20.38	2.08

Figure S2. Experimental and calculated XRD patterns of $Mg_3SiO_4F_2$.

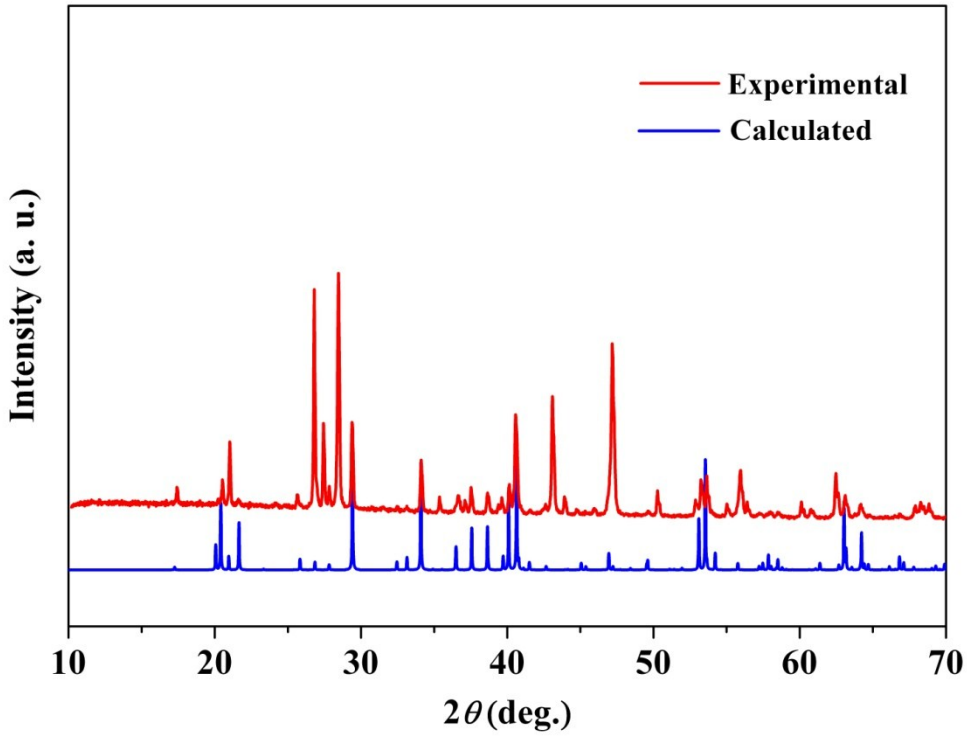

Table S2. (a) Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Mg_5(SiO_4)_2F_2$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	X	Y	Z	U_{eq}	BVS
Mg(1)	5802(3)	4930(4)	3868(2)	5(1)	2.058
Mg(2)	8015(3)	67(4)	6731(2)	4(1)	1.889
Mg(3)	0	5000	5000	5(1)	2.073
Si(1)	2038(3)	761(5)	6442(2)	23(1)	4.197
O(1)	7921(5)	7692(10)	5041(5)	14(1)	1.911
O(2)	3715(6)	2763(9)	2560(4)	8(1)	2.207
O(3)	247(6)	2240(10)	6663(4)	11(1)	2.019
O(4)	2070(5)	-2599(9)	6455(4)	7(1)	2.103
F(1)	6024(4)	2715(7)	5585(3)	8(1)	0.941

Table S2. (b) Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for $Mg_3SiO_4F_2$. 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)	5937(2)	2500	-68(4)	3(1)	1.864
Mg(2)	8667(1)	4297(2)	-103(3)	4(1)	2.058
Si(1)	7805(2)	2500	4193(5)	19(1)	4.129
O(1)	9264(5)	2500	2732(10)	9(1)	1.952
O(2)	7094(3)	3954(4)	2688(7)	9(1)	2.131
O(3)	7794(4)	2500	7570(10)	6(1)	2.075
F(1)	5327(2)	4165(3)	-2722(6)	7(1)	0.961

Table S3. (a) Selected bond distances (Å) and angles (deg) for $Mg_5(SiO_4)_2F_2$.

Mg(1)-F(1)	1.997(4)	F(1)-Mg(1)-O(1)	89.49(17)
Mg(1)-O(2)	1.999(4)	O(2)-Mg(1)-O(1)	171.9(2)
Mg(1)-F(1)#7	2.016(4)	F(1)#7-Mg(1)-O(1)	89.86(16)
Mg(1)-O(4)#4	2.096(4)	O(4)#4-Mg(1)-O(1)	84.22(17)
Mg(1)-O(2)#8	2.096(4)	O(2)#8-Mg(1)-O(1)	74.2(2)
Mg(1)-O(1)	2.120(4)	F(1)#12-Mg(2)-O(1)	91.96(17)
Mg(2)-F(1)#12	2.021(4)	F(1)#12-Mg(2)-O(3)#12	100.21(18)
Mg(2)-O(1)	2.036(4)	O(1)-Mg(2)-O(3)#12	91.56(19)
Mg(2)-O(3)#12	2.048(5)	F(1)#12-Mg(2)-O(2)#7	97.22(17)
Mg(2)-O(2)#7	2.174(4)	O(1)-Mg(2)-O(2)#7	96.02(18)
Mg(2)-O(4)#13	2.175(4)	O(3)#12-Mg(2)-O(2)#7	160.7(2)
Mg(2)-O(3)#14	2.180(5)	F(1)#12-Mg(2)-O(4)#13	87.46(15)
Mg(3)-O(1)	2.057(4)	O(1)-Mg(2)-O(4)#13	175.38(18)
Mg(3)-O(1)#2	2.057(4)	O(3)#12-Mg(2)-O(4)#13	93.05(18)
Mg(3)-O(3)	2.089(4)	O(2)#7-Mg(2)-O(4)#13	79.51(16)
Mg(3)-O(3)#2	2.089(4)	F(1)#12-Mg(2)-O(3)#14	164.51(17)
Mg(3)-O(4)#4	2.113(4)	O(1)-Mg(2)-O(3)#14	98.85(19)
Mg(3)-O(4)#12	2.113(4)	O(3)#12-Mg(2)-O(3)#14	90.60(12)
Si(1)-O(2)#1	1.577(5)	O(2)#7-Mg(2)-O(3)#14	70.76(19)
Si(1)-O(4)	1.565(5)	O(4)#13-Mg(2)-O(3)#14	80.86(16)
Si(1)-O(3)	1.617(5)	O(1)-Mg(3)-O(1)#2	180.0(3)
Si(1)-O(1)#2	1.693(5)	O(1)-Mg(3)-O(3)	103.0(2)
O(2)#1-Si(1)-O(1)#2	102.0(2)	O(1)#2-Mg(3)-O(3)	77.0(2)
O(3)-Si(1)-O(1)#2	102.5(2)	O(1)-Mg(3)-O(3)#2	77.0(2)
F(1)-Mg(1)-O(2)	98.19(17)	O(1)#2-Mg(3)-O(3)#2	103.0(2)
F(1)-Mg(1)-F(1)#7	84.11(16)	O(3)-Mg(3)-O(3)#2	180.000(1)
F(1)-Mg(1)-O(4)#4	91.78(16)	O(1)-Mg(3)-O(4)#4	85.35(16)
O(2)-Mg(1)-O(4)#4	97.98(18)	O(1)#2-Mg(3)-O(4)#4	94.65(16)
F(1)#7-Mg(1)-O(4)#4	172.84(17)	O(3)-Mg(3)-O(4)#4	95.53(16)
F(1)-Mg(1)-O(2)#8	163.28(19)	O(2)-Mg(1)-F(1)#7	88.43(17)
O(2)-Mg(1)-O(2)#8	98.29(13)	O(3)#2-Mg(3)-O(4)#4	84.47(16)
F(1)#7-Mg(1)-O(2)#8	99.16(16)	O(1)-Mg(3)-O(4)#12	94.65(16)
O(4)#4-Mg(1)-O(2)#8	83.15(17)	O(1)#2-Mg(3)-O(4)#12	85.35(16)
O(4)-Si(1)-O(2)#1	115.0(2)	O(3)-Mg(3)-O(4)#12	84.47(16)
O(4)-Si(1)-O(3)	115.9(2)	O(3)#2-Mg(3)-O(4)#12	95.53(16)
O(2)#1-Si(1)-O(3)	104.3(2)	O(4)#4-Mg(3)-O(4)#12	180
O(4)-Si(1)-O(1)#2	115.3(2)		

Note. Symmetry transformations used to generate equivalent atoms:

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

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

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

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

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

#12 x,y+1,z #13 -x+2,y+3/2,-z+3/2

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

Table S3. (b) Selected bond distances (Å) and angles (deg) for $Mg_3SiO_4F_2$.

Mg(1)-F(1)#1	2.002(3)	F(1)#1-Mg(1)-O(3)#3	87.90(13)
Mg(1)-F(1)	2.002(3)	F(1)-Mg(1)-O(3)#3	87.90(13)
Mg(1)-O(1)#2	2.032(5)	O(1)#2-Mg(1)-O(3)#3	177.6(2)
Mg(1)-O(2)	2.157(4)	O(2)-Mg(1)-O(3)#3	79.58(16)
Mg(1)-O(2)#1	2.157(4)	O(2)#1-Mg(1)-O(3)#3	79.58(16)
Mg(1)-O(3)#3	2.200(5)	F(1)#8-Mg(2)-O(2)#9	96.78(14)
Mg(2)-F(1)#8	1.985(3)	F(1)#8-Mg(2)-F(1)#6	83.02(13)
Mg(2)-O(2)#9	1.995(4)	O(2)#9-Mg(2)-F(1)#6	88.72(14)
Mg(2)-F(1)#6	2.020(3)	F(1)#8-Mg(2)-O(2)	165.95(15)
Mg(2)-O(2)	2.093(4)	O(2)#9-Mg(2)-O(2)	97.21(11)
Mg(2)-O(3)#3	2.101(4)	F(1)#6-Mg(2)-O(2)	98.57(14)
Mg(2)-O(1)	2.134(4)	F(1)#8-Mg(2)-O(3)#3	93.50(16)
Si(1)-O(3)	1.570(5)	O(2)#9-Mg(2)-O(3)#3	97.73(15)
Si(1)-O(2)#1	1.619(4)	F(1)#6-Mg(2)-O(3)#3	173.01(14)
Si(1)-O(2)	1.619(4)	O(2)-Mg(2)-O(3)#3	83.34(17)
Si(1)-O(1)	1.645(6)	F(1)#8-Mg(2)-O(1)	91.48(16)
F(1)#1-Mg(1)-F(1)	92.57(18)	O(2)#9-Mg(2)-O(1)	171.42(19)
F(1)#1-Mg(1)-O(1)#2	93.73(14)	F(1)#6-Mg(2)-O(1)	89.96(13)
F(1)-Mg(1)-O(1)#2	93.73(14)	O(2)-Mg(2)-O(1)	74.60(18)
F(1)#1-Mg(1)-O(2)	164.17(15)	O(3)#3-Mg(2)-O(1)	84.05(15)
F(1)-Mg(1)-O(2)	96.58(13)	O(3)-Si(1)-O(2)#1	115.40(17)
O(1)#2-Mg(1)-O(2)	98.52(17)	O(3)-Si(1)-O(2)	115.40(17)
F(1)#1-Mg(1)-O(2)#1	96.58(13)	O(2)#1-Si(1)-O(2)	102.7(3)
F(1)-Mg(1)-O(2)#1	164.17(15)	O(3)-Si(1)-O(1)	114.8(3)
O(1)#2-Mg(1)-O(2)#1	98.52(17)	O(2)#1-Si(1)-O(1)	103.43(18)
O(2)-Mg(1)-O(2)#1	71.8(2)	O(2)-Si(1)-O(1)	103.43(18)

Note. Symmetry transformations used to generate equivalent atoms:

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

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

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

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

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

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

Figure S3. The coordination of cations for $Mg_5(SiO_4)_2F_2$: (a) the $Mg1O_4F_2$ octahedron; (b) the $Mg2O_5F$ octahedron; (c) the $Mg3O_6$ octahedron; (d) the SiO_4 tetrahedron

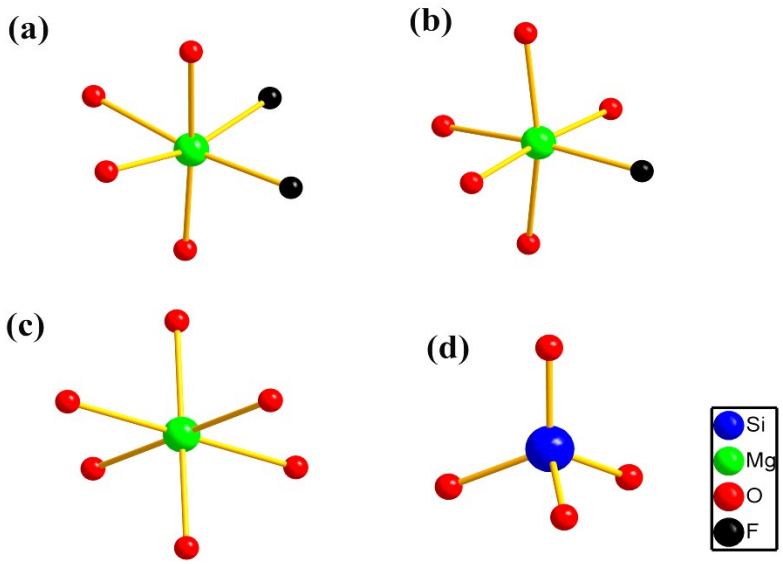

Figure S4. The coordination of cations for $Mg_3SiO_4F_2$: (a) the $Mg1O_4F_2$ octahedron; (b) the $Mg2O_4F_2$ octahedron; (c) the SiO_4 tetrahedron

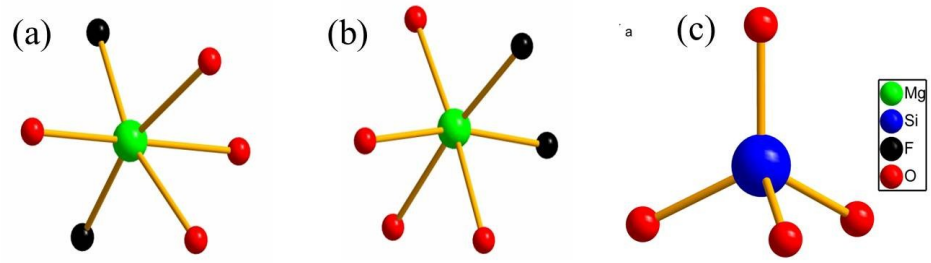

Figure S5. The IR spectrum of $Mg_5(SiO_4)_2F_2$.

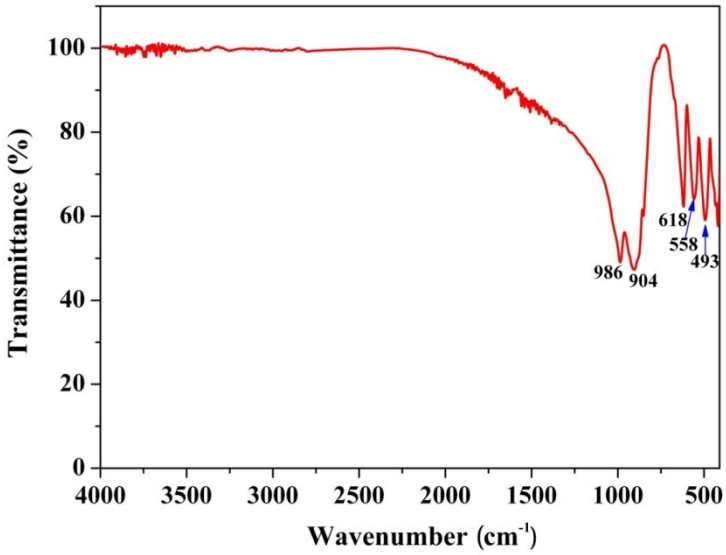

Figure S6. The diffuse reflectance spectrum for $Mg_5(SiO_4)_2F_2$.

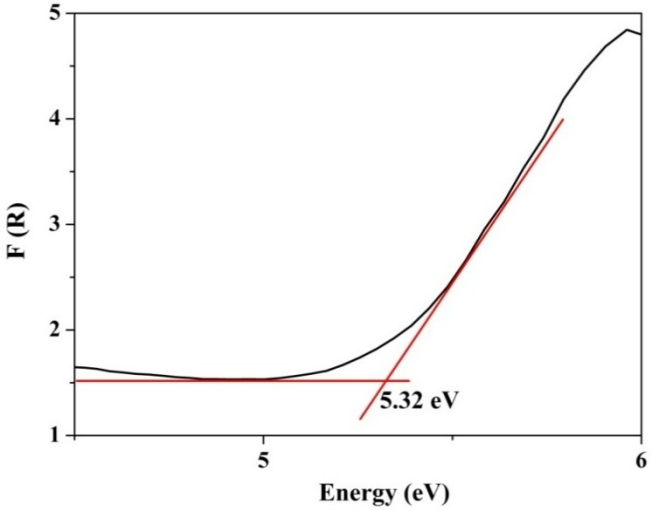

Table S4. (a) The optimized lattice parameters between experimental and theoretical results for $Mg_5(SiO_4)_2F_2$.

	a (Å)	*b*(Å)	*c*(Å)	Alpha	Beta	Gamma
Castep Calculation	7.907(8)	4.7862(7)	10.382(6)	90	109.041(44)	90
Experimental Result	7.774(2)	4.6585(11)	10.254(3)	90	109.516 (15)	90

Table S4. (b) The optimized lattice parameters between experimental and theoretical results for $Mg_3SiO_4F_2$.

	a (Å)	*b*(Å)	*c*(Å)	Alpha	Beta	Gamma
Castep Calculation	10.424(8)	8.862(8)	4.766(3)	90	90	90
Experimental Result	10.268(7)	8.694(6)	4.650(3)	90	90	90

Table S5. (a) The calculated bond lengths in comparison with experimental data for $Mg_5(SiO_4)_2F_2$.

bond type	experiment bond length (Å)	calculation bond length(Å)
Mg(1)-F(1)	1.997(4)	2.0260
Mg(1)-F(1)	2.016(4)	2.0500
Mg(1)-O(1)	2.120(4)	2.1930
Mg(1)-O(2)	1.999(4)	2.0240
Mg(1)-O(2)	2.096(4)	2.1340
Mg(1)-O(4)	2.096(4)	2.1310
Mg(2)-F(1)	2.021(4)	2.0640
Mg(2)-O(1)	2.036(4)	2.0710
Mg(2)-O(3)	2.048(5)	2.0760
Mg(2)-O(2)	2.174(4)	2.2150
Mg(2)-O(4)	2.175(4)	2.2140
Mg(2)-O(3)	2.180(5)	2.2380
Mg(3)-O(1)	2.057(4)	2.1080
Mg(3)-O(3)	2.089(4)	2.1320
Mg(3)-O(4)	2.113(4)	2.1480
Si(1)-O(4)	1.565(5)	1.6290
Si(1)-O(2)	1.577(5)	1.6540
Si(1)-O(3)	1.617(5)	1.6520
Si(1)-O(1)	1.693(5)	1.6660

Table S5. (b) The calculated bond lengths in comparison with experimental data for $Mg_3SiO_4F_2$.

bond type	experiment bond length (Å)	calculation bond length(Å)
Mg(1)-F(1)	2.002(3)	2.0410
Mg(1)-O(1)	2.032(5)	2.0540
Mg(1)-O(2)	2.157(4)	2.2050
Mg(1)-O(3)	2.200(5)	2.2390
Mg(2)-F(1)	1.985(3)	2.0160
Mg(2)-O(2)	1.995(4)	2.0240
Mg(2)-F(1)	2.020(3)	2.0560
Mg(2)-O(2)	2.093(4)	2.1350
Mg(2)-O(3)	2.101(4)	2.1420
Mg(2)-O(1)	2.134(4)	2.2000
Si(1)-O(3)	1.570(5)	1.6290
Si(1)-O(2)	1.619(4)	1.6570
Si(1)-O(1)	1.645(6)	1.6520