Supporting information

Revealing crystal structures and relative dielectric constants of fluorinated silicon oxides†

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I Prediction of Structural Connectivity of SiOF compounds

In general, connectivity of a structure is determined by the central atoms[1]: in a typical 1D-connectivity structure, a central atom is coordinated with two ligands that are shared with other central atoms, leading to the formation of a chain with infinite length; 2D-connectivity structures are often obtained with three or more shared ligands coordinating around a central atom and the elementary motif expands in two directions to form a layer; with central atoms of four or more shared ligands, 3D-connectivity structures can be easily constructed. There are also a few 3D-connectivity structures (e.g., $P3_121$-B_2O_3) in which central atoms only have three shared ligands.

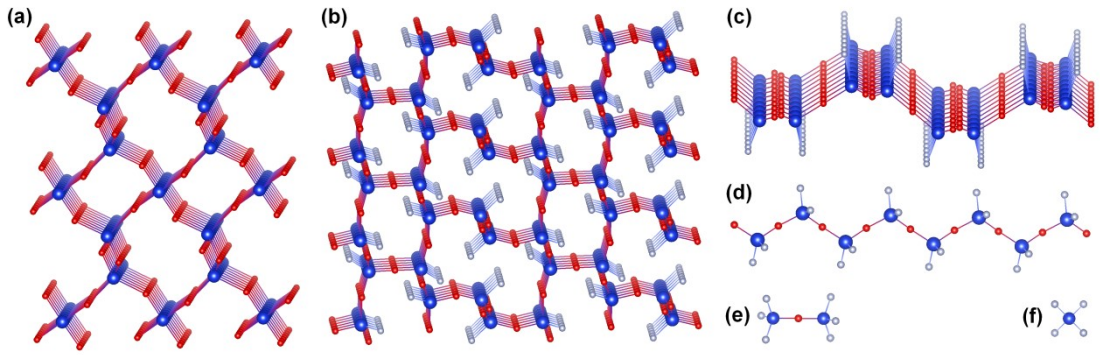

Figure S1. A prediction of structural connectivity of SiOF compounds *vs.* F concentration; (a) 3D-SiO_2 (b) 3D-$Si_2O_3F_2$ (c) 2D-$Si_2O_3F_2$ (d) 1D-$SiOF_2$ (e) 0D-Si_2OF_6 and (f) 0D-SiF_4

According to these guidelines, structural connectivity of SiOF as a function of F concentration can be roughly predicted. As shown in Figure S1(a), if we have a central atom (Si) and four shared ligands (O), we can have 3D-connectivity structures - this is the case of SiO_2. If we have three shared ligands (O) and one unshared ligand (F), we also can have 3D-connectivity structures (but also an increased chance of 2D-connectivity structures). Both 2- and 3-D connectivity are found for $Si_2O_3F_2$, as shown in Figure S1(b) & 1(c). If we have two shared ligands (O) and two unshared

(F), we cannot have 3D-connected structures, but will have 1D-connected structures. This is the case of $SiOF_2$, as shown in Figure S1 (d). If we have no more than one shared ligand (O), then we can only have 0D structures. This is the cases of Si_2OF_6 and SiF_4, as shown in Figure S1(e)&(f). Based on these simple geometric considerations we consider it more likely to find 3D-connectivity SiOF structures in the F concentration range (in at. %) from 0 (SiO_2) to 28.57 ($Si_2O_3F_2$).

II Dynamical stability of thermodynamically stable SiOF compounds

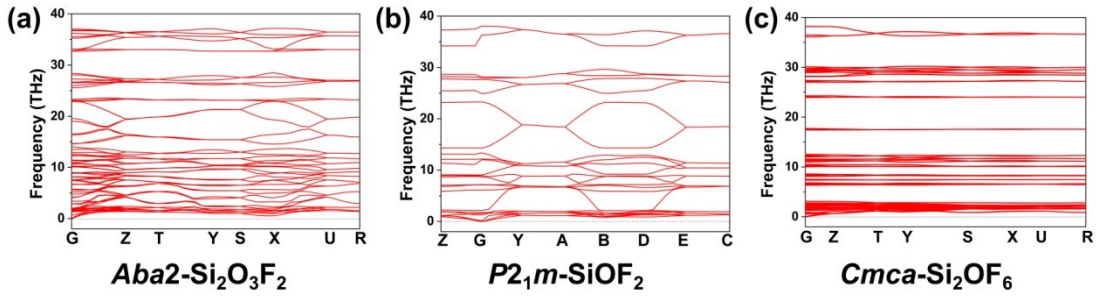

Figure S2 Phonon dispersion curves computed for three thermodynamically stable SiOF compounds; (a) *Aba*2-$Si_2O_3F_2$ (b) $P2_1/m$-SiOF2 and (c) *Cmca*-Si_2OF_6

III Thermodynamical stability of SiOF compounds

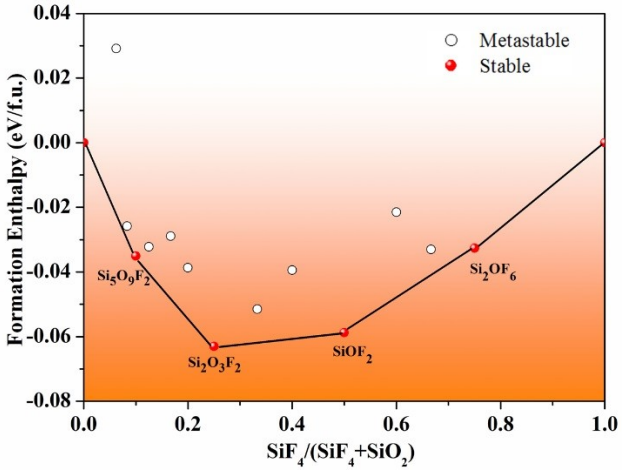

Figure S3 Thermodynamical convex hull constructed for SiO2-SiF4 system at zero temperature and ambient pressure; the stable structures of SiO_2 ($P3_121$) and SiF_4 (I-43m) were used.

Table S1. Detailed information of predicted thermodynamically stable and metastable SiOF structures; the lowest energy structures at a given composition are listed.

Compound	Spg	ΔH (meV/f.u.)	E_{hull} (meV/f.u.)	F ratio (%)	CP-type	Structure Connectivity
SiO_2	*I*-42*d*	0	0	0	SiO_4	3D
$Si_8O_{15}F_2$	*P*1	58.2	68.2	8	SiO_4+SiO_3F	3D
$Si_6O_{11}F_2$	*P*-1	2.6	15.9	10.53	SiO_4+SiO_3F	3D
$Si_5O_9F_2$	*P*1	-7.2	8.8	12.50	SiO_4+SiO_3F	3D
$Si_4O_7F_2$	*P*1	-5.1	14.8	15.38	SiO_4+SiO_3F	3D
$Si_3O_5F_2$	*P*1	-3.1	23.4	20	SiO_4+SiO_3F	3D
$Si_5O_8F_4$	*P*1	-13.9	17.9	23.53	SiO_4+SiO_3F	3D
$Si_2O_3F_2$	*Aba*2	-39.8	0	28.57	SiO_3F	2D
$Si_3O_4F_4$	*P*1	-30.8	10.1	36.36	SiO_3F+SiO_2F_2	2D
$Si_5O_6F_8$	*P*1	-20.8	21.1	42.11	SiO_3F+SiO_2F_2	2D
$Si_2O_2F_4$	$P2_1/m$	-43.3	0	50	SiO_2F_2	1D
$Si_5O_4F_{12}$	*P*-43*m*	-9.1	26.8	57.14	SiO_2F_2+$SiOF_3$	0D
$Si_3O_2F_8$	*C*2	-22.7	8.3	61.54	SiO_2F_2+$SiOF_3$	0D
Si_2OF_6	*Cmca*	-24.9	0	66.67	$SiOF_3$	0D
SiF_4	*I*-43*m*	0	0	80	SiF_4	0D

IV Crystal structure and dynamical stability of *Cc*-$Si_2O_3F_2$

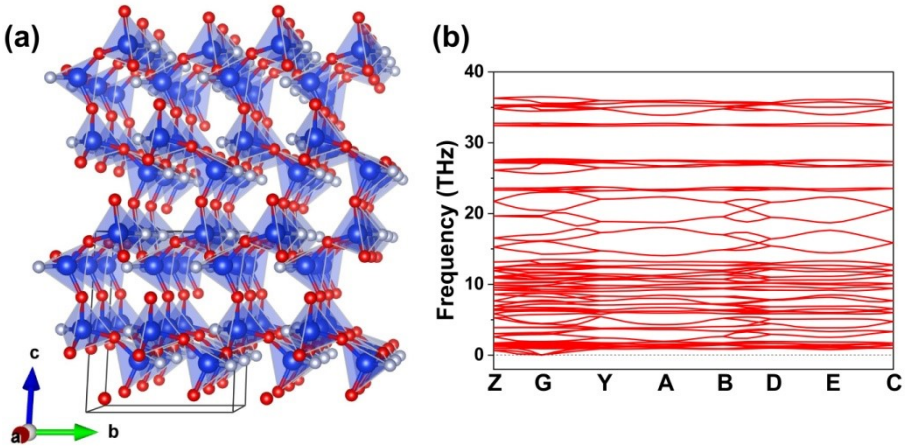

Figure S4 Crystal structure (a) and phonon dispersion curve of *Cc*-$Si_2O_3F_2$

V Test of the semi-empirical model

Table S2 The computed and predicted dielectric constants for seven more predicted metastable SiOF structures; Noting that these seven metastable SiOF compounds are the second lowest energy structures in their compositions.

Compound	Spg	ΔH (meV/atom)	E_{hull} (meV/atom)	V (A^3)	CP-type	k (Predicted)	k (DFPT)
$Si_6O_{11}F_2$	*P*-1	2.8	6.9	47.30	SiO_4+SiO_3F	3.91	3.84
$Si_5O_9F_2$	*C*2	1.7	6.6	48.49	SiO_4+SiO_3F	3.81	3.84
$Si_4O_7F_2$	*C*2	-0.9	5.1	50.35	SiO_4+SiO_3F	3.68	3.79
$Si_3O_5F_2$	*Ibam*	3.2	11.0	56.45	SiO_4+SiO_3F	3.32	3.27
$Si_5O_8F_4$	*P*1	-3.0	6.2	54.70	SiO_4+SiO_3F	3.38	3.43
$Si_2O_3F_2$	*Cm*	-9.8	1.5	54.82	SiO_3F	3.34	3.58
$SiOF_2$	*Ama*2	-6.8	3.9	68.17	SiO_2F_2	2.81	2.81

VI The effect of E_g on ε_e of SiOF compounds

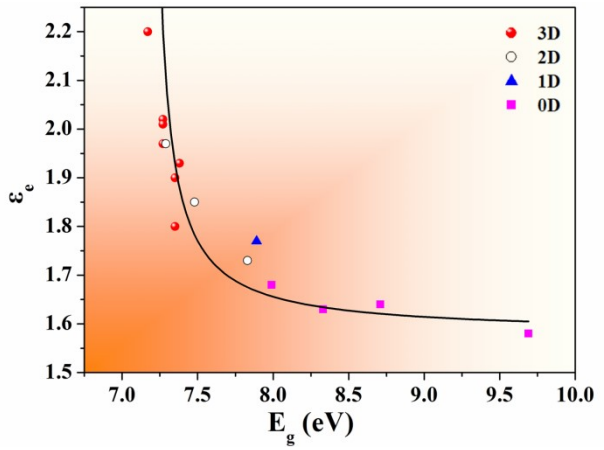

Figure S5 Effect of E_g on ε_e of SiOF compounds

VII Phonon behaviors of three stable SiOF compounds

Table S3 Lattice contributions to ε_L of three SiOF compounds along with SiO_2 and SiF_4; only those higher than 0.03 are listed.

I-42*d*-SiO_2		*Aba*2-$Si_2O_3F_2$		*P*2$_1$/*m*-$SiOF_2$		*Cmca*-Si_2OF_6		*I*-43*m*-SiF_4	
(ω < 500 cm^{-1})									
ω(cm^{-1})	ε_L	ω(cm^{-1})	ε_L	ω(cm^{-1})	ε_L	ω(cm^{-1})	ε_L	ω(cm^{-1})	ε_L
422	0.40	211	0.04	284	0.03	363	0.12	351	0.30
442	0.57	272	0.06	366	0.35	373	0.12		
		409	0.43	397	0.13	380	0.08		
		427	0.16	403	0.09	384	0.03		
SUM	0.85	SUM	0.69	SUM	0.60	SUM	0.41	SUM	0.30
(ω > 500 cm^{-1})									
752	0.07	874	0.09	818	0.05	935	0.06	947	0.17
1047	0.21	1092	0.17	915	0.08	952	0.04		
1055	0.39	1104	0.16	1134	0.14	1193	0.11		
				1204	0.04				
SUM	0.67	SUM	0.42	SUM	0.31	SUM	0.21	SUM	0.17

References

1 B. Kesanli and W. Lin, Coord. Chem. Rev., 2003, 246(1-2), 305-326.