Electronic Supplementary Information for

Anion Ratio-Directed Design of $CaB_4O_5F_4$ and $CaB_6O_8F_4$: $[BO_3]$ / $[BO_2F_2]$ Hybridization Tailoring Deep-Ultraviolet Nonlinear Optical Performance

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Table S1. All predicted $CaB_4O_5F_4$ structures with E_{hull} values <0.1 eV/atom.

No.	Formula	Symmetry	Space groups	Anion groups	Anionic framework dimensions	E_{hull} (eV/atom)
1	$Ca_4B_{16}O_{20}F_{16}$	CS	*C*2/*c*	2*[BO_3] +2*[BO_2F_2]	2D	0.011
2	$Ca_2B_8O_{10}F_8$	CS	$P\bar{1}$	2*[BO_3] +2*[BO_2F_2]	2D	0.013
3	$Ca_2B_8O_{10}F_8$	NCS	*Pnn*2	2*[BO_3] +2*[BO_2F_2]	3D	0.030
4	$Ca_2B_8O_{10}F_8$	CS	$P\bar{1}$	2*[BO_3] +2*[BO_2F_2]	1D	0.040
5	$Ca_2B_8O_{10}F_8$	CS	$P\bar{1}$	2*[BO_3] +2*[BO_2F_2]	2D	0.060
6	$Ca_2B_8O_{10}F_8$	CS	$P\bar{1}$	2*[BO_3] +2*[BO_2F_2]	1D	0.063
7	$Ca_2B_8O_{10}F_8$	NCS	*Pc*	2*[BO_3] +2*[BO_2F_2]	2D	0.066
8	$Ca_2B_8O_{10}F_8$	NCS	$P2_1$	2*[BO_3] +2*[BO_2F_2]	2D	0.067
9	$Ca_2B_8O_{10}F_8$	CS	$P\bar{1}$	[BO_3] +[BO_4] +2*[BO_2F_2]	2D	0.071
10	$Ca_2B_8O_{10}F_8$	NCS	*Pc*	2*[BO_3] +2*[BO_2F_2]	2D	0.073
11	$Ca_2B_8O_{10}F_8$	NCS	$P2_1$	2*[BO_3] +2*[BO_2F_2]	2D	0.073
12	$Ca_2B_8O_{10}F_8$	NCS	$P2_1$	2*[BO_3] +2*[BO_2F_2]	2D	0.076
13	$Ca_2B_8O_{10}F_8$	CS	$P\bar{1}$	2*[BO_3] +2*[BO_2F_2]	1D	0.078
14	$Ca_2B_8O_{10}F_8$	NCS	*Pc*	2*[BO_3] +2*[BO_2F_2]	2D	0.078
15	$Ca_4B_{16}O_{20}F_{16}$	NCS	*Cc*	2*[BO_3] +2*[BO_2F_2]	3D	0.078
16	$Ca_2B_8O_{10}F_8$	CS	$P\bar{1}$	2*[BO_3] +2*[BO_2F_2]	1D	0.079
17	$Ca_2B_8O_{10}F_8$	NCS	$P2_1$	2*[BO_3] +2*[BO_2F_2]	2D	0.079
18	$Ca_2B_8O_{10}F_8$	CS	$P\bar{1}$	2*[BO_3] +2*[BO_2F_2]	2D	0.082
19	$Ca_2B_8O_{10}F_8$	CS	$P\bar{1}$	2*[BO_3] +2*[BO_2F_2]	2D	0.083
20	$Ca_2B_8O_{10}F_8$	CS	$P\bar{1}$	2*[BO_3] +2*[BO_2F_2]	2D	0.083
21	$Ca_2B_8O_{10}F_8$	CS	$P\bar{1}$	2*[BO_3] +2*[BO_2F_2]	1D	0.086
22	$Ca_2B_8O_{10}F_8$	NCS	$P2_1$	2*[BO_3] +[BO_3F]	2D	0.086
23	$Ca_2B_8O_{10}F_8$	NCS	*Pc*	2*[BO_3] +2*[BO_2F_2]	1D	0.090
24	$Ca_2B_8O_{10}F_8$	NCS	$P2_1$	2*[BO_3] +[BO_3F] +[BOF_3]	2D	0.091
25	$Ca_2B_8O_{10}F_8$	CS	$P\bar{1}$	2*[BO_3] +2*[BO_2F_2]	2D	0.093
26	$Ca_2B_8O_{10}F_8$	NCS	*Pc*	2*[BO_3] +[BO_3F] +[BOF_3]	2D	0.094

27	$Ca_2B_8O_{10}F_8$	NCS	$P2_1$	6*[BO_3] +2*[BO_3F]	2D	0.096

Table S2. All predicted $CaB_6O_8F_4$ structures with E_{hull} values <0.1 eV/atom.

No.	Formula	Symmetry	Space groups	Anion groups	Anionic framework dimensions	E_{hull} (eV/atom)
1	$Ca_2B_{12}O_{16}F_8$	NCS	$C2$	2*[BO_3] +[BO_2F_2]	1D	0.026
2	$Ca_2B_{12}O_{16}F_8$	NCS	Pc	2*[BO_3] +[BO_2F_2]	2D	0.046
3	$Ca_2B_{12}O_{16}F_8$	CS	$P2_1/c$	2*[BO_3] +[BO_2F_2]	1D	0.050
4	$Ca_2B_{12}O_{16}F_8$	NCS	$P2$	2*[BO_3] +[BO_2F_2]	2D	0.066
5	$Ca_2B_{12}O_{16}F_8$	NCS	Pc	2*[BO_3] +[BO_2F_2]	2D	0.072
6	$Ca_2B_{12}O_{16}F_8$	NCS	Pc	2*[BO_3] +2*[BO_4] +2*[BO_2F_2]	2D	0.073

Table S3. The crystallographic data of $CaB_4O_5F_4$(I-IV) and $CaB_6O_8F_4$, including cell parameters, fractional coordinates, bond lengths.

$CaB_4O_5F_4$-I ($C2/c$)					
Cell parameter					
a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
9.9295	8.4662	8.5104	90	114.7699	90
Fractional coordinate					
Atoms		x/a	y/b	z/c	
Ca1		0	0.3624	1.25	
B1		0.79343	0.68209	1.28010	
B2		0.36976	0.45374	1.24252	
O1		0.26659	0.34869	1.24844	
O2		0.65587	0.61343	1.26854	
O3		0	0.89452	1.25	
F1		0.90857	0.65585	1.45559	
F2		0.84567	0.60523	1.16819	
Bond lengths (Å)					
Ca1- O1		2.655	B1-O1	1.45	
Ca1- O2		2.581	B1-O2	1.44	
Ca1- O2		2.581	B1-F1	1.468	
Ca1- O1		2.656	B1-F2	1.418	
Ca1- F1		2.285	B2-O1	1.371	
Ca1- F1		2.285	B2-O2	1.364	
Ca1- F2		2.483	B2-O3	1.373	
Ca1- F2		2.483			

$CaB_4O_5F_4$-II ($P\bar{1}$)					
Cell parameter					
a (Å)	*b* (Å)	*c* (Å)	*α* (˚)	*β* (˚)	*γ* (˚)
6.5119	6.5208	8.4513	70.1333	71.3184	80.9561
Fractional coordinate					
Atoms	*x*/*a*	*y*/*b*	*z*/*c*		
Ca1	0.36679	0.13891	0.75238		
B1	0.47844	0.61221	0.72200		
B2	0.82691	0.41750	0.75889		
B3	0.08650	0.67825	0.74484		
B4	0.89336	0.02844	0.77567		
O1	0.61765	0.41737	0.75511		
O2	0.27121	0.54340	0.73518		
O3	0.89619	0.60718	0.75312		
O4	0.08551	0.88664	0.74977		
O5	0.96305	0.23360	0.76631		
F1	0.56849	0.75508	0.54293		
F2	0.45603	0.74105	0.83287		
F3	0.25628	0.06238	0.04872		
F4	0.76956	0.05792	0.65796		
Bond lengths (Å)					
Ca1- O1	2.637	B1-F1	1.465		
Ca1- O2	2.578	B1-F2	1.465		
Ca1- O4	2.657	B2-O1	1.373		
Ca1- O5	2.578	B2-O3	1.362		
Ca1- F1	2.265	B2-O5	1.371		
Ca1- F2	2.472	B3-O2	1.371		
Ca1- F3	2.269	B3-O3	1.364		
Ca1- F4	2.511	B3-O4	1.373		
B1-O1	1.447	B4-O4	1.438		
B1-O2	1.440	B4-O5	1.448		
B4-F3	1.47	B4-F4	1.418		

$CaB_4O_5F_4$-III (*Pnn*2)					
Cell parameter					
a (Å)	*b* (Å)	*c* (Å)	*α* (˚)	*β* (˚)	*γ* (˚)
5.0255	9.1129	6.8102	90	90	90
Fractional coordinate					
Atoms	*x*/*a*	*y*/*b*	*z*/*c*		

Ca1	0	0.5	0.72345
B1	0.34923	0.37974	0.30839
B2	0.54707	0.29291	0.98205
O1	0.60268	0.71874	0.16159
O2	0.64842	0.14748	0.94078
O3	0.5	0.5	0.34674
F1	0.61917	0.65352	0.82652
F2	0.76721	0.39492	0.99399
Bond lengths (Å)			
Ca1- O1	2.648	B2-O1	1.376
Ca1- O1	2.648	B2-O3	1.358
Ca1- O2	2.463	B1-O3	1.365
Ca1- O2	2.463	B2-O1	1.439
Ca1- F1	2.473	B3-O3	1.439
Ca1- F1	2.472	B3-F1	1.435
Ca1- F2	2.384	B3-F3	1.447
Ca1- F2	2.384		

$CaB_4O_5F_4$-IV ($P\bar{1}$)					
Cell parameter					
a (Å)	*b* (Å)	*c* (Å)	*α* (˚)	*β* (˚)	*γ* (˚)
4.4196	9.3701	9.7535	63.3899	89.5219	89.7503
Fractional coordinate					
Atoms		*x*/*a*	*y*/*b*	*z*/*c*	
Ca1		0.26666	0.99768	0.75163	
B1		0.70266	0.21794	0.83727	
B2		0.80264	0.64085	0.23821	
B3		0.70042	0.78056	0.66220	
B4		0.80547	0.36194	0.26549	
O1		0.89331	0.65516	0.75017	
O2		0.61427	0.23496	0.29224	
O3		0.39047	0.23195	0.79014	
O4		0.10252	0.65868	0.25426	
O5		0.67950	0.50118	0.25222	
F1		0.71550	0.18814	0.99746	
F2		0.20246	0.93698	0.15743	
F3		0.79103	0.93202	0.66553	
F4		0.27769	0.18116	0.49998	
Bond lengths (Å)					

Ca1- O2	2.456	B1-F2	1.487
Ca1- O3	2.452	B2-O3	1.388
Ca1- F1	2.283	B2-O4	1.356
Ca1- F2	2.430	B2-O5	1.368
Ca1- F2	2.683	B3-O1	1.394
Ca1- F3	2.451	B3-O2	1.444
Ca1- F3	2.621	B3-F3	1.491
Ca1- F4	2.281	B3-F4	1.460
B1-O3	1.445	B4-O1	1.356
B1-O4	1.395	B4-O2	1.387
B1-F1	1.460	B4-O5	1.368

$CaB_6O_8F_4$-I (*C*2)					
Cell parameter					
a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)
10.4878	8.3208	6.9613	90	130.8993	90
Fractional coordinate					
Atoms		*x*/*a*	*y*/*b*	*z*/*c*	
Ca1		0	0.5725	0	
B1		0.78737	0.04049	0.69584	
B2		0.20540	0.80136	0.50955	
B3		0.28837	0.75914	0.92584	
O1		0.24460	0.86599	0.72131	
O2		0.83463	0.10076	0.91275	
O3		0.67526	0.38574	0.31610	
O4		0.69630	0.13506	0.47487	
F1		0.15093	0.74400	0.92405	
F2		0.42497	0.84114	0.15393	
Bond lengths (Å)					
Ca1- O1	2.662		B2-O1	1.355	
Ca1- O1	2.662		B2-O3	1.360	
Ca1- O4	2.555		B2-O4	1.397	
Ca1- O4	2.554		B3-O1	1.474	
Ca1- F1	2.432		B3-O2	1.428	
Ca1- F1	2.433		B3-F1	1.439	
Ca1- F2	2.565		B3-F2	1.435	
Ca1- F2	2.564		B1-O2	1.364	
B1-O3	1.405		B1-O4	1.34	

$CaB_6O_8F_4$-II (*Pc*)					
Cell parameter					
a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)
5.1298	10.7150	11.6699	90	119.2582	90
Fractional coordinate					
Atoms		*x*/*a*	*y*/*b*	*z*/*c*	
Ca1		-0.39690	-0.12773	0.24054	
B1		1.30112	-0.01632	0.94811	
B2		1.10524	-0.68340	0.81508	
B3		1.35672	-0.30888	0.72630	
B4		0.26925	-0.18920	0.52555	
B5		1.25044	-0.45305	0.85404	
B6		1.34648	-0.23902	0.91768	
O1		0.37438	-0.28257	0.61652	
O2		-0.61954	-0.14162	0.00164	
O3		1.15967	-0.56458	0.87204	
O4		1.27700	-0.35619	0.93925	
O5		1.07785	-0.78067	0.89654	
O6		-0.65769	-0.93488	0.05484	
O7		1.31088	-0.42887	0.75246	
O8		1.37696	-0.21318	0.80922	
F1		0.34000	-0.27657	0.28490	
F2		-0.00333	-0.98069	0.33982	
F3		-0.17096	-0.30450	0.19371	
F4		0.48354	-0.02825	0.39292	
Bond lengths (Å)					
Ca1-O2	2.447	B3-O1	1.357		
Ca1-O5	2.424	B3-O7	1.368		
Ca1-O6	2.815	B3-O8	1.379		
Ca1-F1	2.306	B4-O1	1.364		
Ca1-F2	2.369	B4-O5	1.375		
Ca1-F3	2.418	B4-O6	1.378		
Ca1-F4	2.396	B5-O3	1.336		
B1-O2	1.453	B5-O4	1.397		
B1-O6	1.449	B5-O7	1.388		
B1-F2	1.452	B6-O2	1.383		
B1-F4	1.452	B6-O4	1.362		
B2-O3	1.400	B6-O8	1.377		
B2-O5	1.463	B2-F3	1.438		

B2-F1	1.474	

Table S4. Calculated band gap, birefringence, the shortest SHG phase-matching wavelengths (λ_{PM}) and the effective SHG coefficients for the predicted $CaB_4O_5F_4$ (V-XI) bulk structures.

Formula	**Space groups**	**HSE06（eV）**	**GGA（eV）**	**Birefringence (@1064 nm)**	**Shortest λ_{PM} (nm)**	**SHG effect (pm/V)**	**E_{hull} (eV/atom)**
$CaB_4O_5F_4$-V	$P2_1$	7.57	6.03	0.092	167	d_{16}=0.098, d_{22}= -0.185 (0.47×KDP), d_{23}= -0.091	0.067
$CaB_4O_5F_4$-VI	$P2_1$	8.02	6.31	0.097	157	d_{16}=0.0735, d_{14}=0.134 (0.34×KDP), d_{23}= -0.134	0.073
$CaB_4O_5F_4$-VII	$P2_1$	7.34	6.00	0.074	184	d_{16}=0.233 (0.6×KDP), d_{22}=0.056, d_{23}=0.208	0.076
$CaB_4O_5F_4$-VIII	Pc	7.50	6.00	0.071	185	d_{11}= -0.360, d_{15}=0.237, d_{12}=0.418, d_{13}=-0.134, d_{24}= -0.086, d_{33}= -0.591 (1.5×KDP)	0.078
$CaB_4O_5F_4$-IX	Cc	8.20	6.52	0.048	226	d_{11}= -0.342（0.88×KDP）, d_{15}=0.303, d_{12}= -0.22, d_{13}=0.213, d_{24}= -0.107	0.078
$CaB_4O_5F_4$-X	$P2_1$	7.65	6.17	0.045	226	d_{16}= -0.482(1.23×KDP), d_{14}=0.247, d_{22}= -0.261, d_{23}=0.268	0.079
$CaB_4O_5F_4$-XI	Pc	7.65	5.95	0.026	264	d_{11}= -0.455（1.17×KDP）, d_{15}=0.120, d_{12}= -0.204,	0.090

						d_{13}=0.093, d_{24}=0.054, d_{33}= -0.116	

Table S5. Calculated band gap, birefringence, the shortest SHG phase-matching wavelengths (λ_{PM}) and the effective SHG coefficients for the predicted $CaB_6O_8F_4$ (II-VI) bulk structures.

Crystals	**Space groups**	**HSE06 （eV）**	**GGA （eV）**	**Birefringence (@1064 nm)**	**Shortest λ_{PM} (nm)**	**SHG effect (pm/V)**	**E_{hull} (eV/atom)**
$CaB_6O_8F_4$-III	$P2_1/c$	7.16	5.80	0.074	/	/	0.050
$CaB_6O_8F_4$-IV	$P2$	7.04	5.76	0.018	345	d_{16}= -0.408, d_{14}=0.704 (1.8×KDP), d_{22}=0.340, d_{23}=0.508	0.066
$CaB_6O_8F_4$-V	Pc	6.76	5.52	0.059	215	d_{11}=0.295, d_{15}=0.412 (1×KDP), d_{12}=-0.193, d_{24}=-0.395	0.072
$CaB_6O_8F_4$-VI	Pc	5.65	6.94	0.053	215	d_{11}=-0.48 (1.23×KDP) d_{12}=-0.333 d_{13}=-0.242, d_{24}=0.06 d_{33}=0.166	0.073

Table S6. SHG response and the shortest phase-matching wavelength of the synthesized deep-UV materials.

Crystal	Space group	Absorption edge (nm)	SHG effect (×KDP)	Birefringence (@1064 nm)	Shortest phase-matching wavelength (nm)	Refs.
$KBe_2BO_3F_2$	*R*32	147	1.26	0.077	161	1
$RbBe_2BO_3F_2$	*R*32	152	1.15	0.073	170	2
$NH_4Be_2BO_3F_2$	*R*32	153	1.2	0.057@400 nm	173.9	3
$NaBe_2BO_3F_2$	*C*2	155	1.4	0.091@200 nm	185	4
$BaBe_2BO_3F_3$	$P6_3$	<185	0.1	0.081@200 nm	196	5
Be_2BO_3F	*C*2	150	0.1	0.0915	180	6
Be_2BO_3F	*R*32	144.8	2.3	0.0989	146	3
$NH_4B_4O_6F$	$Pna2_1$	156	3	0.1171	158	7
NaB_4O_6F	*C*2	<180	0.9	0.12	166	8
RbB_4O_6F	$Pna2_1$	<190	0.8	0.102	165	9
CsB_4O_6F	$Pna2_1$	155	1.9	0.114	171.6	10
$CsKB_8O_{12}F_2$	*P*321	<190	1.9	0.105	170	11
$CaB_5O_7F_3$	$Cmc2_1$	<180	2	0.07	183	12
$SrB_5O_7F_3$	$Cmc2_1$	<180	1.6	0.072@589 nm	180	13
$MgB_5O_7F_3$	$Cmc2_1$	<200	2.4	0.07	189	14
$Li_2B_6O_9F_2$	*Cc*	<190	0.9	0.07	192	15
$CsAlB_3O_6F$	$Pna2_1$	<190	2	0.091	182	16
$RbAlB_3O_6F$	$Pna2_1$	<200	0.2	0.095	174	17
$C(NH_2)_3BF_4$	*R*3*m*	193	3.6	0.11	193.2	18
$Cs_2Al_2(B_3O_6)_2O$	$P6_3$	185	0.5	0.136@177.3 nm	185	19
$Sr_2Be_2B_2O_7$	*P*2*c*	155	3.8	0.062@589 nm	200	20
$SrB_8O_{15}H_4$	$P2_1$	<200	1.8	0.109	185	21
$CaB_8O_{15}H_4$	$P2_1$	<200	2	0.093	174	21
$[C(NH_2)_3]_2[B_3O_3F_4(OH)]$	P_1	190	0.9	0.173	190	22
$[C(NH_2)_3]_2[B_3O_3F_4(OH)]$	P_1	195	1.4	0.161	195	23
$Cs_2KY(B_3O_6)_2$	*Pc*2	< 190	4.8	0.078@1064	<200	24

Table S7. $\Delta\rho^b$, group contribution and corresponding birefringence of $CaB_4O_5F_4$-I, II and $CaB_6O_8F_4$-I, II.

Structure	**Group**	$\Delta\rho^b$	**Group contribution**	**Birefringence**
$CaB_4O_5F_4$-I	$[BO_3]$	0.0187	87.04%	0.084
	$[BO_2F_2]$	0.0035	16.46%	
	$[CaO_4F_4]$	-0.0008	-3.5%	
$CaB_4O_5F_4$-II	$[BO_3]$	0.0191	87%	0.086
	$[BO_2F_2]$	0.0006	2.61%	
	$[CaO_4F_4]$	0.0023	10.38%	
$CaB_4O_5F_4$-III	$[BO_3]$	0.0017	44.88%	0.035
	$[BO_2F_2]$	0.0007	17.44%	

	$[CaO_4F_4]$	0.0014	37.68%	
$CaB_4O_5F_4$-IV	$[BO_3]$	0.0166	78.36%	0.07
	$[BO_2F_2]$	0.0029	13.50%	
	$[CaO_2F_6]$	0.0017	8.14%	
$CaB_6O_8F_4$-I	$[BO_3]$	0.04936	91.70%	0.106
	$[BO_2F_2]$	0.0039	7.20%	
	$[CaO_4F_4]$	0.0006	1.10%	
$CaB_6O_8F_4$-II	$[BO_3]$	0.0147	67.21%	0.083
	$[BO_2F_2]$	0.0054	24.44%	
	$[CaO_3F_4]$	0.0018	8.36%	

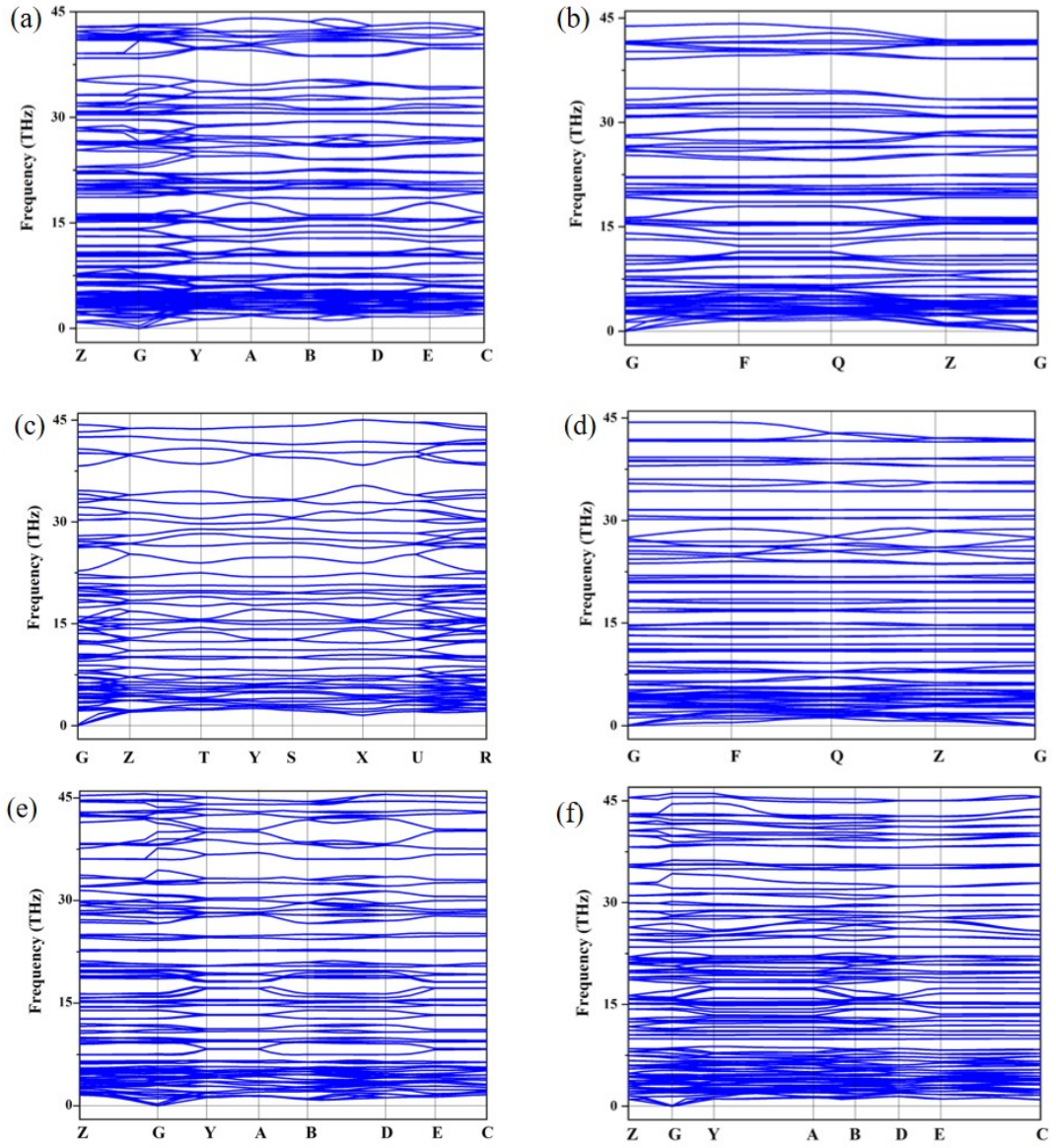

Figure S1. Phonon dispersion spectra of $CaB_4O_5F_4$-I (a), II (b), III (c), IV(d), $CaB_6O_8F_4$-I (e) and II (f).

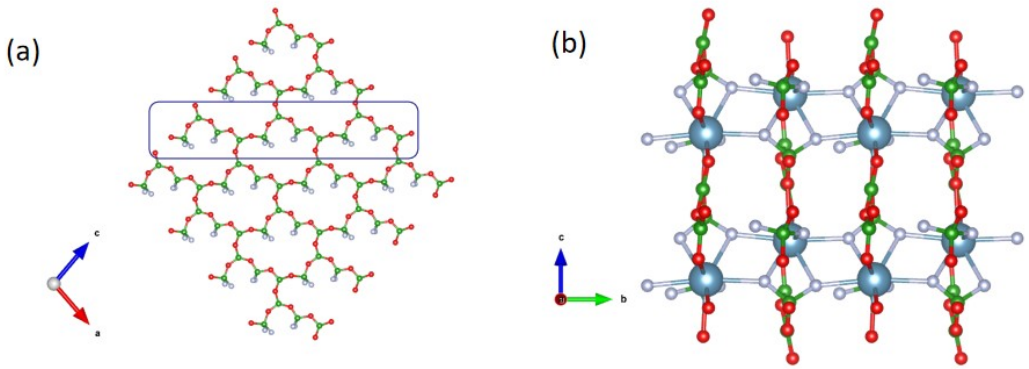

Figure S2. (a) $[B_4O_5F_4]_\infty$ chain and (b) three-dimensional structure of $CaB_4O_5F_4$-VI.

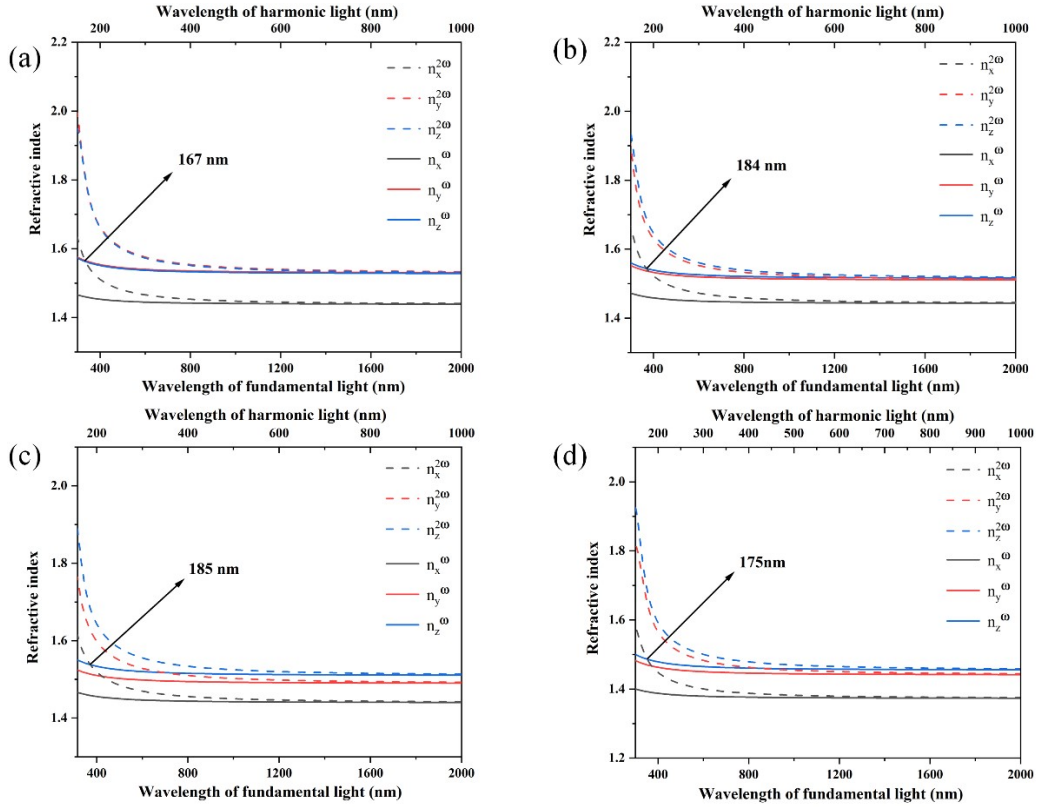

Figure S3. Refractive index dispersion curves and shortest SHG PM wavelengths of $CaB_4O_5F_4$-V (a), VII (b), VIII(c), and $CaB_6O_8F_4$-II (d).

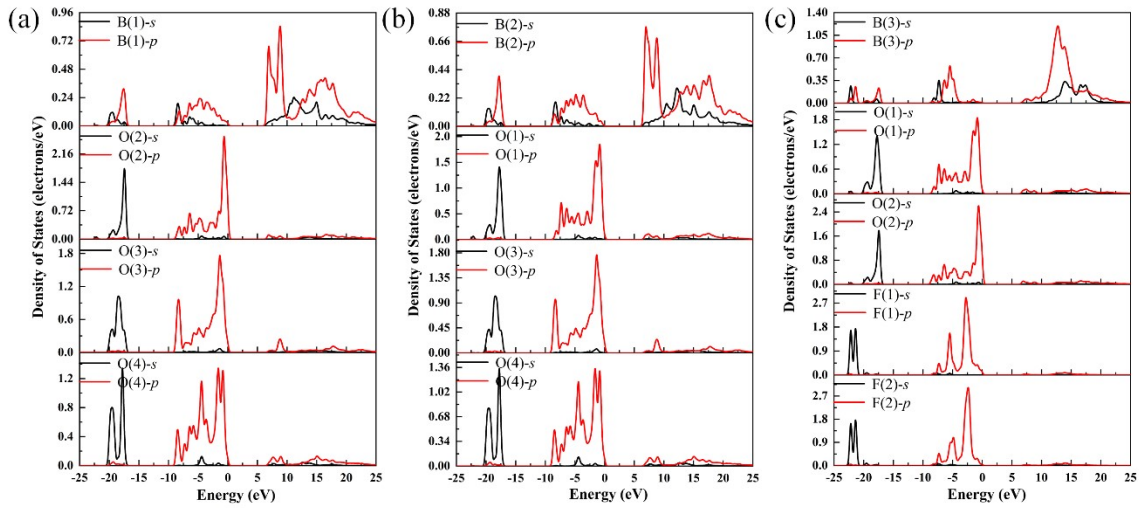

Figure S4. PDOS plot of each atom in the $[B(1)O_3]$, $[B(2)O_3]$and $[B(3)O_2F_2]$ groups of $CaB_6O_8F_4$-I.

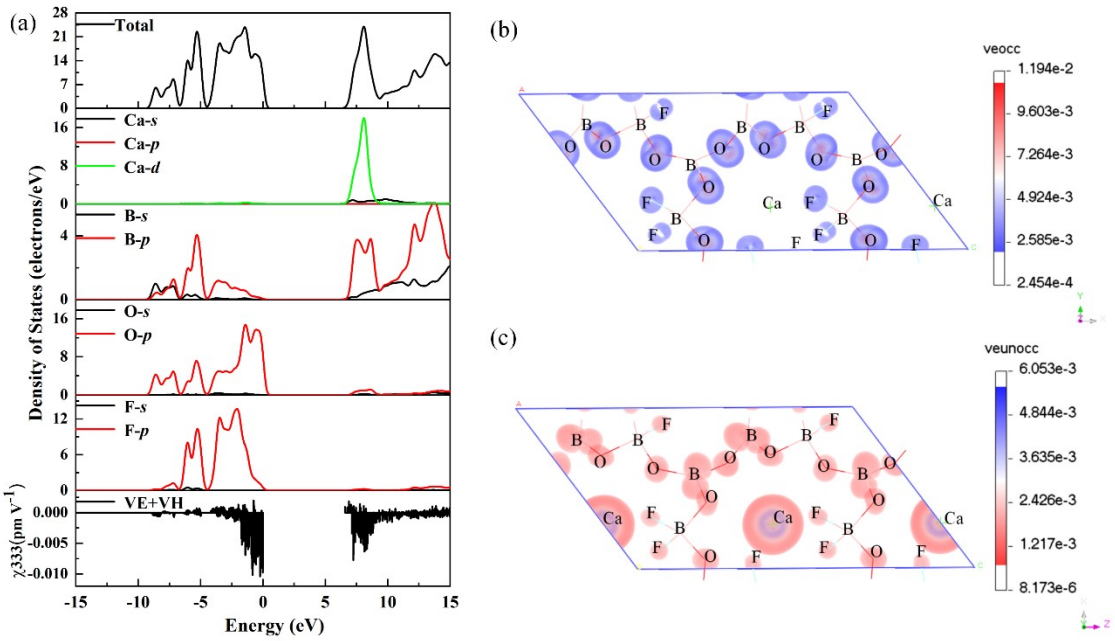

Figure S5. Occupied and unoccupied SHG-density of $CaB_4O_5F_4$-III in VE process.

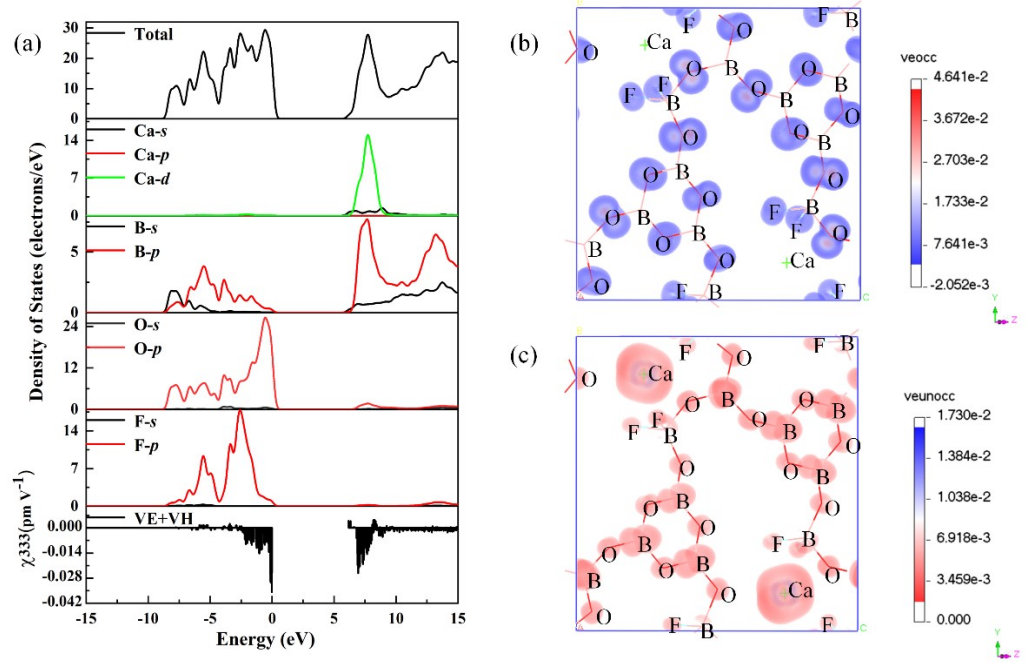

Figure S6. Occupied and unoccupied SHG-density of $CaB_6O_8F_4$-II in VE process.

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