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Enhanced Birefringence and Suppressed Second Harmonic Generation Response Mechanism in Nonlinear Optical Materials via Structural Fine-Tuning

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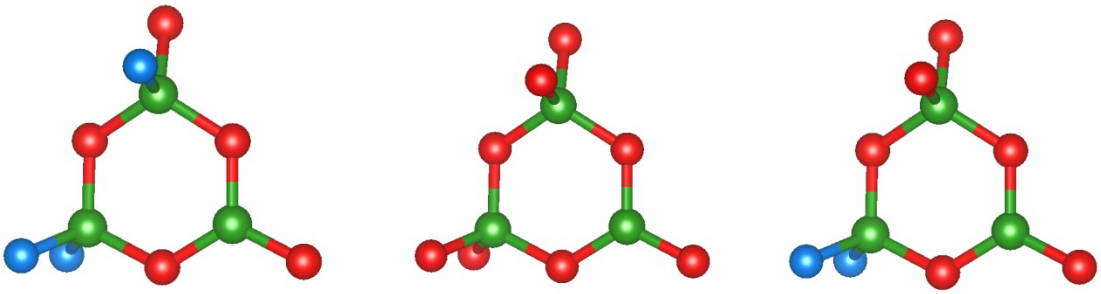
Figure S1. Two cluster models by substituting F with O for $B_3O_5F_3$, namely B_3O_8 and $B_3O_6F_2$



$B_3O_5F_3$ B_3O_8 $B_3O_6F_2$

Figure S2. The LDA band gap of $Li_2B_3O_4F_3$ at 5 (a), 10 (b), 15 (c) and 20 GPa.

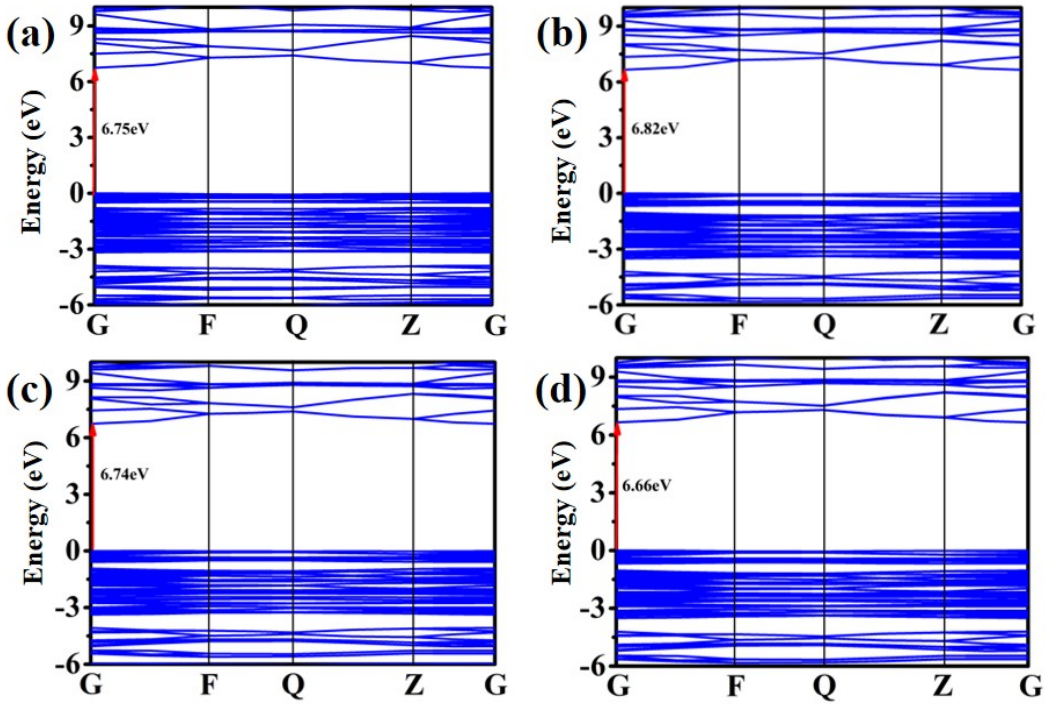


Figure S3. The PDOS for $Li_2B_3O_4F_3$ at 5 (a), 10 (b), 15 (c) and 20 GPa.

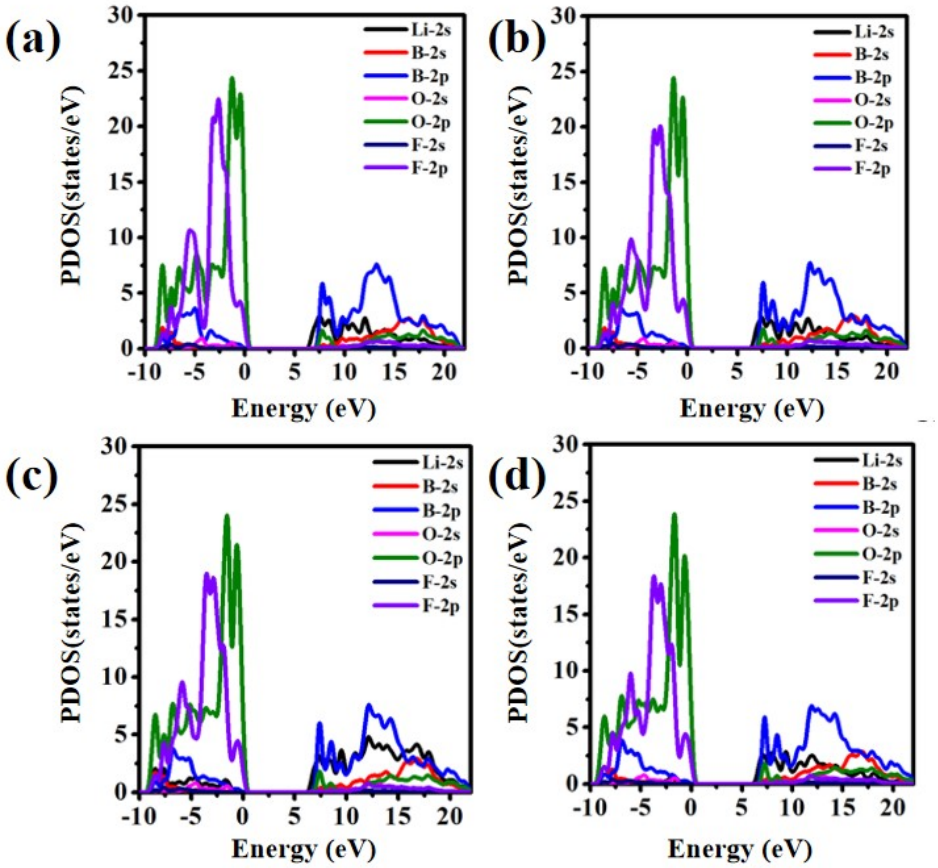


Figure S4. The phase matching wavelength of $Li_2B_3O_4F_3$ at 0, 5, 10, 15 GPa.

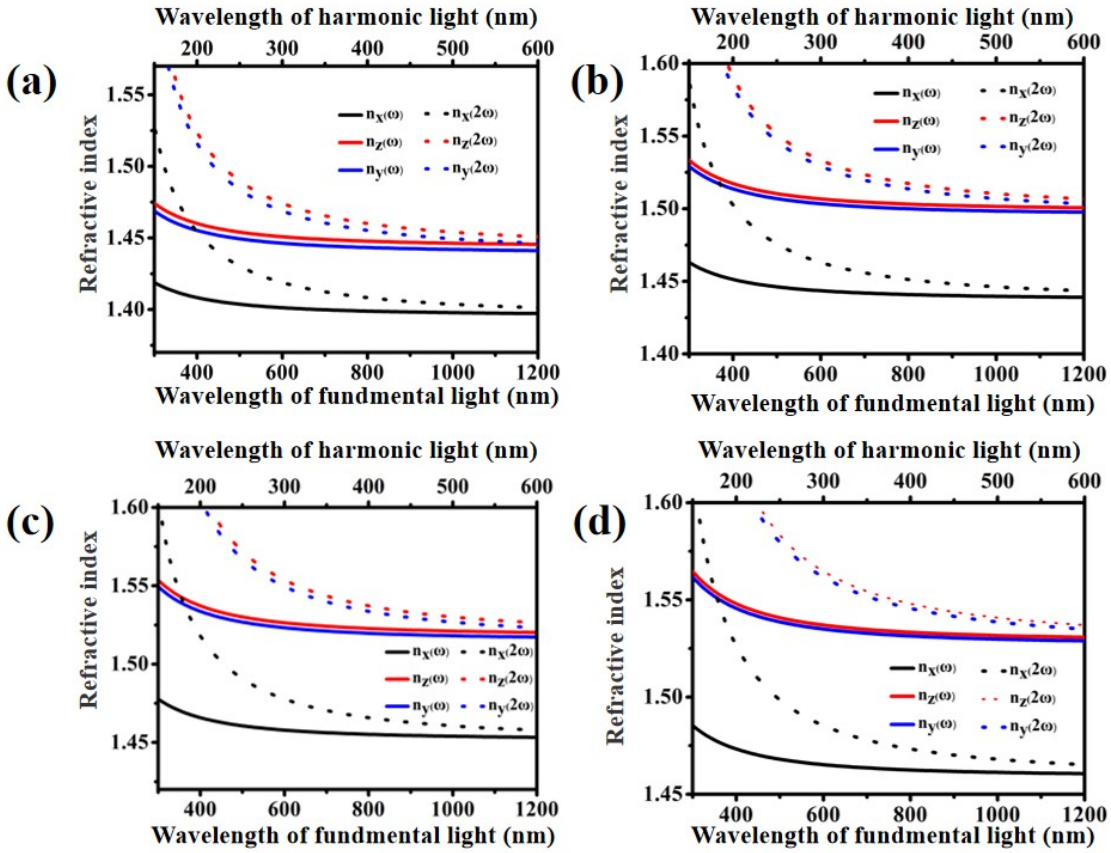


Table S1. The HOMO-LUMO energy gaps of B_3O_8, B_3O_7F, and $B_3O_5F_3$.

Module	HOMO	LUMO	Band gap (eV)
B_3O_8	1.155	1.316	4.37
B_3O_7F	0.991	1.165	4.72
$B_3O_5F_3$	0.594	0.836	6.58

Table S2. The bond lengths (Å) and bond angles (°) of single BO_3, BO_3F and BO_2F_2 group under pressure.

BO_3	B-O1	B-O2	B-O3	O1-B-O2	O1-B-O3	O2-B-O3
0 GP	1.361	1.352	1.347	120.731	122.151	117.117
5 GP	1.363	1.353	1.341	121.002	122.756	116.240
10 GPa	1.363	1.351	1.342	120.990	122.780	116.226
15 GPa	1.364	1.352	1.343	120.953	123.030	116.016
20 GPa	1.365	1.351	1.343	120.935	123.161	115.903

BO_3F	B-O1	B-O2	B-O3	B-F	O1-B-O2	O1-B-O3	O1-B-F	O2-B-O3	O2-B-F	O3-B-F
0GPa	1.437	1.432	1.435	1.435	112.993	106.220	109.383	113.070	107.248	107.793
5GPa	1.446	1.430	1.437	1.417	112.476	107.211	109.835	113.647	107.662	105.780
10GPa	1.451	1.430	1.440	1.406	112.842	107.592	110.084	114.637	106.621	104.726
15GPa	1.452	1.432	1.445	1.393	113.384	108.166	109.162	115.461	106.311	103.772
20GPa	1.454	1.433	1.449	1.382	113.961	108.623	108.384	116.254	105.819	102.919

BO_2F_2	B-O1	B-O2	B-F1	B-F2	O1-B-O2	O1-B-F1	O1-B-F2	O2-B-F1	O2-B-F2	F1-B-F2
0GPa	1.417	1.436	1.436	1.419	114.595	108.743	110.078	109.269	109.052	104.63
5GPa	1.413	1.433	1.451	1.419	114.760	109.264	112.018	110.214	108.375	101.386
10GPa	1.414	1.433	1.459	1.410	114.988	110.552	111.901	110.709	108.440	99.108
15GPa	1.413	1.433	1.473	1.397	115.670	110.617	111.614	111.299	108.109	98.134
20GPa	1.413	1.434	1.485	1.386	116.210	110.897	111.287	112.249	107.707	96.743

Table S3. The single BO_3F and BO_2F_2 group dipole moment directions at different pressure.

BO_3F	**BO_2F_2**	**cosα**	**α**
(0.7767, -0.9891, -0.7304)	(-0.4474, 0.8519, -1.9094)	0.0657	86°
(-1.0616, 1.3232, -2.4057)	(1.0732, -1.0826, -0.6515)	-0.2059	101°
(1.5566, -1.0917, -0.5335)	(-1.6069, 1.4633, -2.6719)	-0.3931	113°
(2.0526, -1.1318, -0.6669)	(-1.9189, 1.5183, -2.9044)	-0.4020	114°
(2.4173, -1.1154, -0.7060)	(-2.3597, 1.5100, -3.140)	-0.446	117°