Electronic Supplementary Information

Prediction of Ternary Fluorooxoborates with Coplanar Triangle Units $[BO_xF_{3-x}]^{x-}$ From First-Principles

Zhonglei Wei, [ab] Wenyao Zhang, [ab] Hao Zeng, [a] Hao Li, [ab] Zhihua Yang, [a*] and Shilie Pan [a*]

[a]CAS Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics and Chemistry, CAS; Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40-1 South Beijing Road, Urumqi 830011, China.
[b]Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.
E-mail: zhyang@ms.xjb.ac.cn
slpan@ms.xjb.ac.cn

Contents

1. **Computational methods**
2. **Table S1**. Crystallographic data of the predicted $B_2O_2F_2$ (I-Ⅹ) crystal structure.
3. **Table S2**. A summary of ICSD collection codes of the known ternary oxyfluoride materials $M_xO_yF_z$.
4. **Table S3**. The ICOHP values (in eV/bond) are listed to show the corresponding interactions in Figure S2.
5. **Table S4**. The formation enthalpies (eV/atom) under 0 K of the first 5 good structures with lower energy obtained from USPEX code.
6. **Figure S1**. The phonon spectra of $B_2O_2F_2$.
7. **Figure S2**. The crystal orbital Hamilton population (COHP) analysis of structure Ⅰ, Ⅲ, and Ⅹ bonding interactions based on DFT plane-wave calculations.
8. **Figure S3**. The coordination architectures of fluorine atoms (F) in the known fluorooxoborates and predicted structures.
9. **Figure S4**. The interlayer spacing of the structure Ⅰ, Ⅲ and $KBe_2BO_3F_2$.
10. **Reference**

Computational methods

The first-principles calculations are performed by the psuedopotential methods implemented in the CASTEP package [1--2] based on the density functional theory (DFT). The optimized norm-conserving pseudopotentials [3-4] are used to simulate ion-electron interactions for all constituent elements. The exchange-correlation functional is approximated using the generalized gradient approximation (GGA) as parametrized by Perdew−Burke−Ernzerhof (PBE). [5] Kinetic energy cutoff of 850 eV is chosen with Monkhorst-Pack k-point meshes spanning 0.04/$Å^3$ in the Brillouin zone. The cell parameters and the atomic positions in the unit cells of all crystals are fully optimized using BFGS method. The phonon spectrum of the stable compound was calculated using the linear response method. The convergence thresholds between optimization cycles for energy change, maximum force, maximum stress, and maximum displacement are set as 5.0×10^{-6} eV/atom, 0.01 eV/Å, 0.02 GPa, and 5.0×10^{-4} Å, respectively. And the hybrid HSE06 functional implemented in Pwmat code [6a] was adopted for more accurate bandgap value, HSE_alpha default value 0.25 and NCPP-SG15-PBE pseudopotential was used in all calculations. [6b] The empty bands were set as 3 times that of valence bands in the calculation to ensure the convergence of optical properties.

Structure search method in this paper is implemented within Random Searching Algorithm,[7] certain crystal cell parameter and elements are given for structures, the final structure is derived from natural transition of energy evolution. In order to obtain the lowest energy structure for experimental synthesis, we make the effort to explore minimum potential energies structure within $B_2O_2F_2$, and to our best knowledge, the result indicates that the structure-Ⅰ *Cc* phase in this paper is the lowest energy structure within using genetic algorithm (GA), which is an excellent way in the crystal structure prediction software USPEX. [8] The searching the lowest energy structures within $B_2O_2F_2$ was implemented in the USPEX code through genetic algorithm. Structure prediction calculation were performed at 0 GPa, to speed up the process, we take structure-Ⅰ (Cc phase) as seed structure, each generation contained 60 structures, depending on system size. The initial generation contain 80 structures, the convergence criterion is 20 generation. All structures were relaxed, and the results are shown in Table S4.

Table S1. The crystallographic data of $B_2O_2F_2$ Ⅰ~Ⅹ in prediction.

$B_2O_2F_2$ - Ⅰ (Z=2)						
Cc (9)						
Unit cell parameters	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ(°)
	5.6081	5.3215	c=8.5860	90	154.1932	90
Fractional coordinates	x/a	y/b	z/c			
B	0.64296	-0.35830	0.56202			
O	0.83325	-0.15181	0.74865			
F	1.27379	-0.09081	0.68934			

$B_2O_2F_2$ - Ⅱ (Z=4)						
*C*2/*c* (15)						
Unit cell parameters	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ(°)
	10.1411	5.2225	4.3038	90	74.3269	90
Fractional coordinates	x/a	y/b	z/c			
B	0.36967	0.11689	1.15859			
O	0.37022	0.09699	1.47509			
F	0.37409	0.35067	1.03428			

$B_2O_2F_2$ - Ⅲ (Z=2)						
$P2_1$ (4)						
Unit cell parameters	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ(°)
	5.4880	4.2425	4.7742	90	79.0899°	90
Fractional coordinates	x/a	y/b	z/c			
B1	0.31806	0.95486	0.39300			
B2	0.93242	0.43226	0.12370			
O1	0.77741	0.31242	0.35891			
O2	0.00381	0.24481	0.88773			
F1	0.73459	0.75188	0.66840			

F2	0.48203	0.80377	0.19907

$B_2O_2F_2$ - Ⅳ molecular crystal (Z=4)						
P-1 (2)						
Unit cell parameters	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ(°)
	5.5026	6.5293	6.7834	87.1609	70.6584	97.3439

Fractional coordinates	x/a	y/b	z/c
B	0.00452	0.13928	0.25984
B	0.55266	0.36451	0.21553
B	0.55859	0.28365	0.84967
B	0.07691	0.22021	0.60654
O	0.89561	0.93961	0.27219
O	0.50194	0.55844	0.25037
O	0.57339	0.26449	0.04336
O	0.10080	0.22380	0.40155
F	0.05466	0.25836	0.08153
F	0.38707	0.88008	0.26014
F	0.96480	0.60304	0.30671
F	0.60117	0.26017	0.37053

$B_2O_2F_2$ - Ⅴ (Z=1)						
Pmn2_1 (31)						
Unit cell parameters	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ(°)
	2.4768	4.4132	4.1500	90	90	90

Fractional coordinates	x/a	y/b	z/c
B	0.50000	0.62294	0.04867
O	0.50000	0.49320	0.38801
F	1.00000	0.07376	0.56332

$B_2O_2F_2$ - Ⅵ (Z=6)

Pnma (62)

Unit cell parameters	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ(°)
	8.1549	7.8786	4.8907	90	90	90

Fractional coordinates	x/a	y/b	z/c
B	0.04820	0.25000	0.39321
B	0.33817	0.40466	0.33102
O	0.24516	0.25000	0.36255
O	0.49089	0.39973	0.24264
F	0.51712	0.25000	0.83066
F	0.26416	0.54798	0.40681

$B_2O_2F_2$ - Ⅶ (Z=2)

*P*2 (3)

Unit cell parameters	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ(°)
	6.9489	3.9955	3.9225	90	94.0939	90

Fractional coordinates	x/a	y/b	z/c
B	0.09372	0.09145	0.28673
B	0.63730	0.46215	0.76543
O	0.00000	0.21066	0.00000
O	0.00000	0.88432	0.50000
O	0.73530	0.23325	0.59353
F	0.50000	0.28668	0.00000
F	0.50000	0.63889	0.50000
F	0.27806	0.70287	0.03819

<table>
<tr><th colspan="7">$B_2O_2F_2$ - Ⅷ (Z=2)</th></tr>
<tr><td colspan="7">$P2$ (3)</td></tr>
<tr><td rowspan="2">Unit cell parameters</td><td>a (Å)</td><td>b (Å)</td><td>c (Å)</td><td>α (°)</td><td>β (°)</td><td>γ(°)</td></tr>
<tr><td>6.5281</td><td>3.9617</td><td>3.9745</td><td>90</td><td>90.8235</td><td>90</td></tr>
<tr><td colspan="7"></td></tr>
<tr><td>Fractional coordinates</td><td colspan="2">x/a</td><td colspan="2">y/b</td><td colspan="2">z/c</td></tr>
<tr><td>B</td><td colspan="2">0.62405</td><td colspan="2">0.46319</td><td colspan="2">0.26030</td></tr>
<tr><td>B</td><td colspan="2">0.12665</td><td colspan="2">0.01006</td><td colspan="2">0.79246</td></tr>
<tr><td>O</td><td colspan="2">1.00000</td><td colspan="2">0.83310</td><td colspan="2">1.00000</td></tr>
<tr><td>O</td><td colspan="2">0.50000</td><td colspan="2">0.33480</td><td colspan="2">0.50000</td></tr>
<tr><td>O</td><td colspan="2">0.74921</td><td colspan="2">0.25841</td><td colspan="2">0.07914</td></tr>
<tr><td>F</td><td colspan="2">0.50000</td><td colspan="2">0.67604</td><td colspan="2">1.00000</td></tr>
<tr><td>F</td><td colspan="2">0.00000</td><td colspan="2">0.17315</td><td colspan="2">0.50000</td></tr>
<tr><td>F</td><td colspan="2">0.24979</td><td colspan="2">0.75978</td><td colspan="2">0.58154</td></tr>
</table>

<table>
<tr><th colspan="7">$B_2O_2F_2$ - Ⅸ (Z=2)</th></tr>
<tr><td colspan="7">$P222_1$ (17)</td></tr>
<tr><td rowspan="2">Unit cell parameters</td><td>a (Å)</td><td>b (Å)</td><td>c (Å)</td><td>α (°)</td><td>β (°)</td><td>γ(°)</td></tr>
<tr><td>2.4768</td><td>4.4132</td><td>4.1500</td><td>90</td><td>90</td><td>90</td></tr>
<tr><td colspan="7"></td></tr>
<tr><td>Fractional coordinates</td><td colspan="2">x/a</td><td colspan="2">y/b</td><td colspan="2">z/c</td></tr>
<tr><td>B</td><td colspan="2">0.28932</td><td colspan="2">0.74269</td><td colspan="2">1.12382</td></tr>
<tr><td>O</td><td colspan="2">0.50000</td><td colspan="2">0.07794</td><td colspan="2">0.75000</td></tr>
<tr><td>O</td><td colspan="2">0.42043</td><td colspan="2">0.50000</td><td colspan="2">1.00000</td></tr>
<tr><td>F</td><td colspan="2">1.00000</td><td colspan="2">0.58191</td><td colspan="2">1.25000</td></tr>
<tr><td>F</td><td colspan="2">0.92048</td><td colspan="2">1.00000</td><td colspan="2">1.50000</td></tr>
</table>

<table>
<tr><th colspan="7">$B_2O_2F_2$ - Ⅹ (Z=2)</th></tr>
<tr><td colspan="7">$I2_12_12_1$ (24)</td></tr>
<tr><td rowspan="2">Unit cell parameters</td><td>a (Å)</td><td>b (Å)</td><td>c (Å)</td><td>α (°)</td><td>β (°)</td><td>γ(°)</td></tr>
<tr><td>4.0229</td><td>3.8929</td><td>6.5359</td><td>90</td><td>90</td><td>90</td></tr>
<tr><td colspan="7"></td></tr>
<tr><td>Fractional coordinates</td><td colspan="2">x/a</td><td colspan="2">y/b</td><td colspan="2">z/c</td></tr>
<tr><td>B</td><td colspan="2">0.50000</td><td colspan="2">0.75000</td><td colspan="2">0.39973</td></tr>
<tr><td>O</td><td colspan="2">0.25000</td><td colspan="2">0.57791</td><td colspan="2">0.50000</td></tr>
</table>

F	0.16570	1.00000	0.75000

Table S2. A brief summary (ICSD Collection Code) for known ternary oxyfluoride materials $M_xO_yF_z$ among Ⅲ A to Ⅶ A.

Compounds/ (ICSD Collection Code)	Other type crystal	Molecular crystal
[BOF]	/	/
[AlOF]	36556; 260261	
[SiOF]	159577; 171499	
[GaOF]	/	/
[GeOF]	250513	
[AsOF]	/	/
[InOF]	2521	
[SnOF]	948; 78356; 409393	
[SbOF]	21099;62476;67157; 78849;431207;431209;	
[TeOF]	1275; 2173; 2174; 82162;88415	
[COF]		163001; 249217 401780; 414408
[NOF]		411510
[POF]		63246; 248122;250498
[SOF]		48148; 62968;66514
[ClOF]		412426
[SeOF]		12110
[BrOF]		50199

[IOF]		4076;201202;280804

Table S3. The ICOHP values (in eV/bond) are listed to show the corresponding interactions in Figure S2.

	I		Ⅲ		X	
	Length	ICOHP	Length	ICOHP	Length	ICOHP
B-O	1.349	-12.15	1.374	-11.92	1.368	-11.88
	1.354	-12.39	1.372	-12.46		
			1.370	-11.57		
			1.344	-11.37		
B-F	1.342	-12.76	1.328	-12.79	1.53	-7.82
	2.444	-0.74	1.338	-11.87		
			2.366	-0.87		
O-F	2.279	-0.236	2.313	-0.13	2.33	-0.134
	2.337	-0.216	2.373	-0.11	2.35	-0.1

Table S4. The formation enthalpies (eV/atom) under 0 K of the first 5 good structures[*] with lower energy obtained from USPEX code.

	Enthalpies	Space group
1	-7.0513	*Cc*
2	-7.0220	*Cm*
3	-7.0093	*Pmc*2
4	-7.005	*C*2/*m*
5	-6.996	$P2_1$

[*] Eventually produce 60 structures in the goodstructures file, we ruled out structure with *P*1 space-group and choose the first 5 structures.

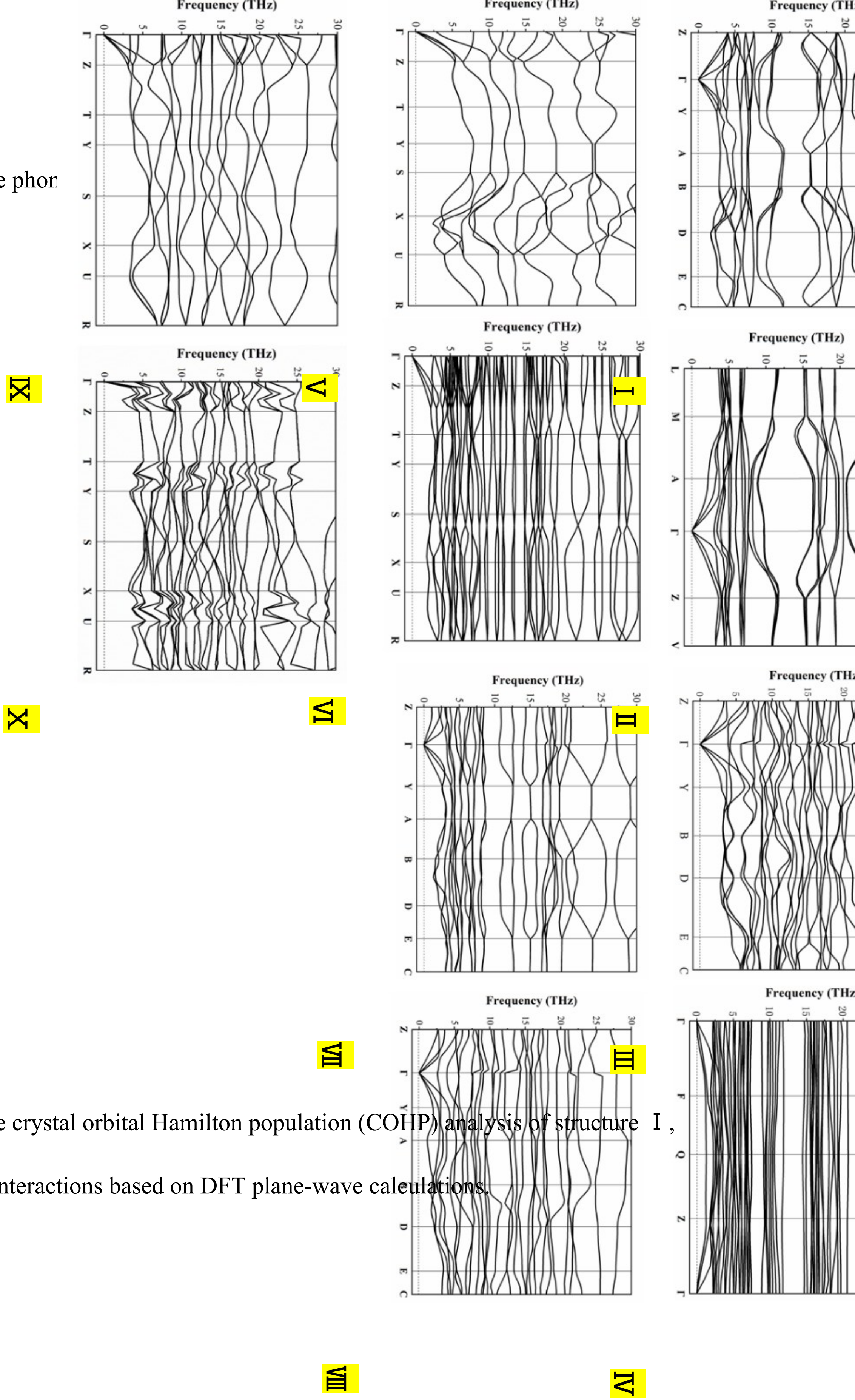
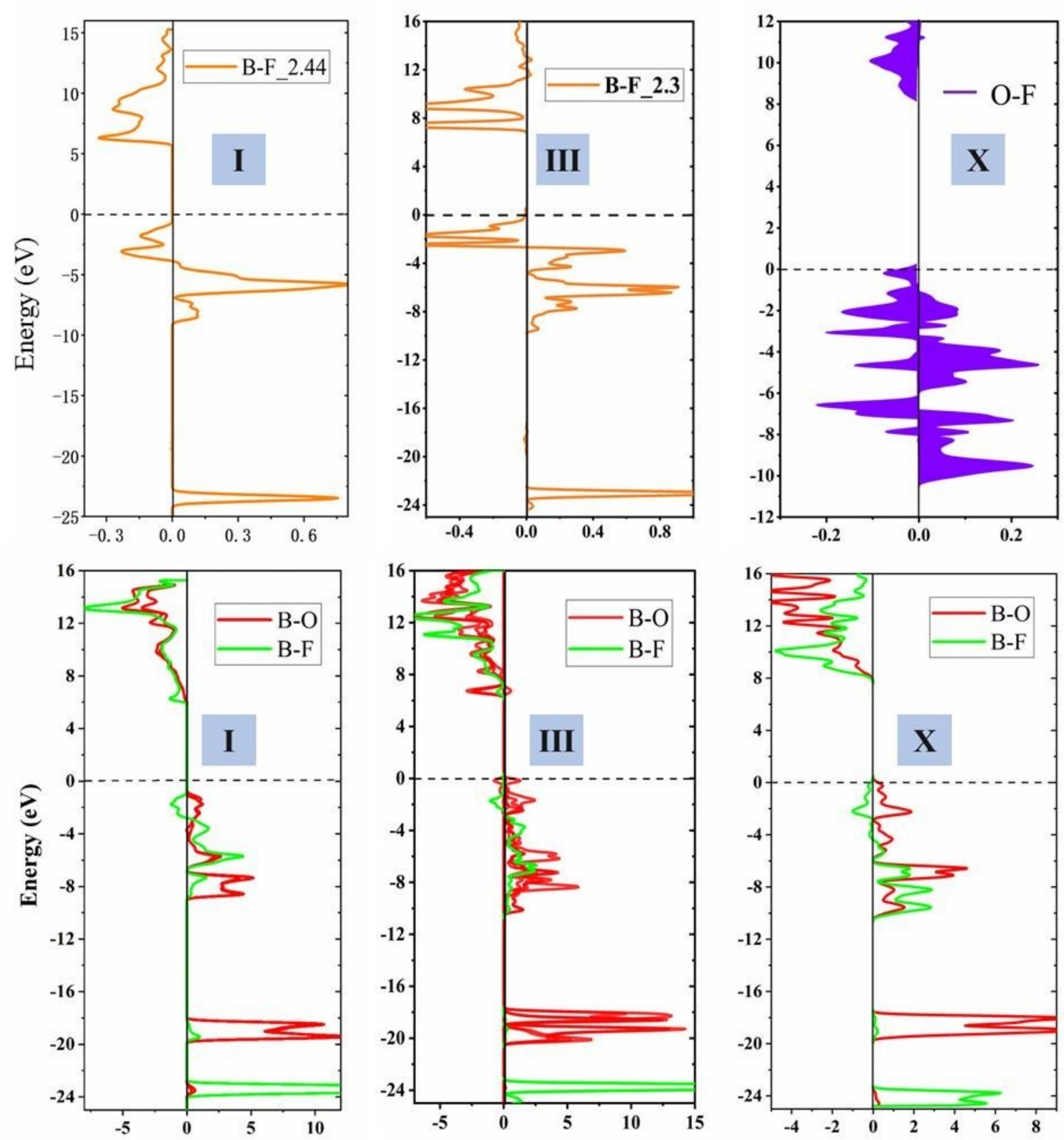


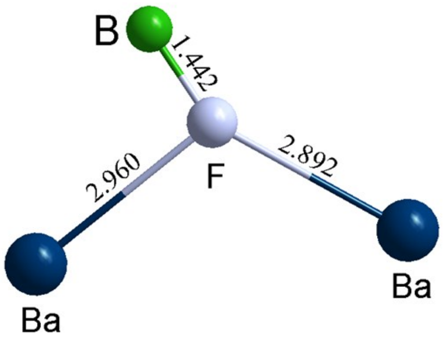
Figure S1. The phon

Figure S2. The crystal orbital Hamilton population (COHP) analysis of structure Ⅰ, Ⅲ, Ⅹ bonding interactions based on DFT plane-wave calculations.



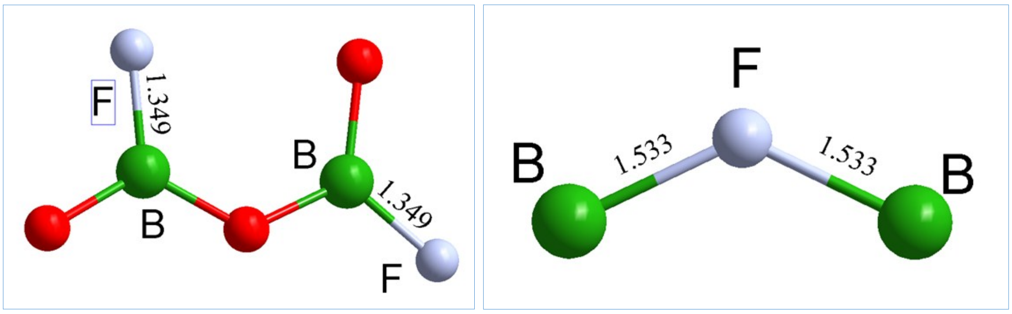
Negative value indicates antibonding interaction and positive value indicates bonding interaction.

Figure S3. The coordination architectures of fluorine atom (F) in the known structures and predicted structures.



Bond length in conventional fluorooxoborates, B-F covalent interaction and Ba-F ionic interaction. Partial structure sketch map of alkaline-earth metal fluorooxoborate $BaB_4O_6F_2$.[9]

This structural characteristic is consistent with those of alkali-metal and transition metal fluorooxoborates.

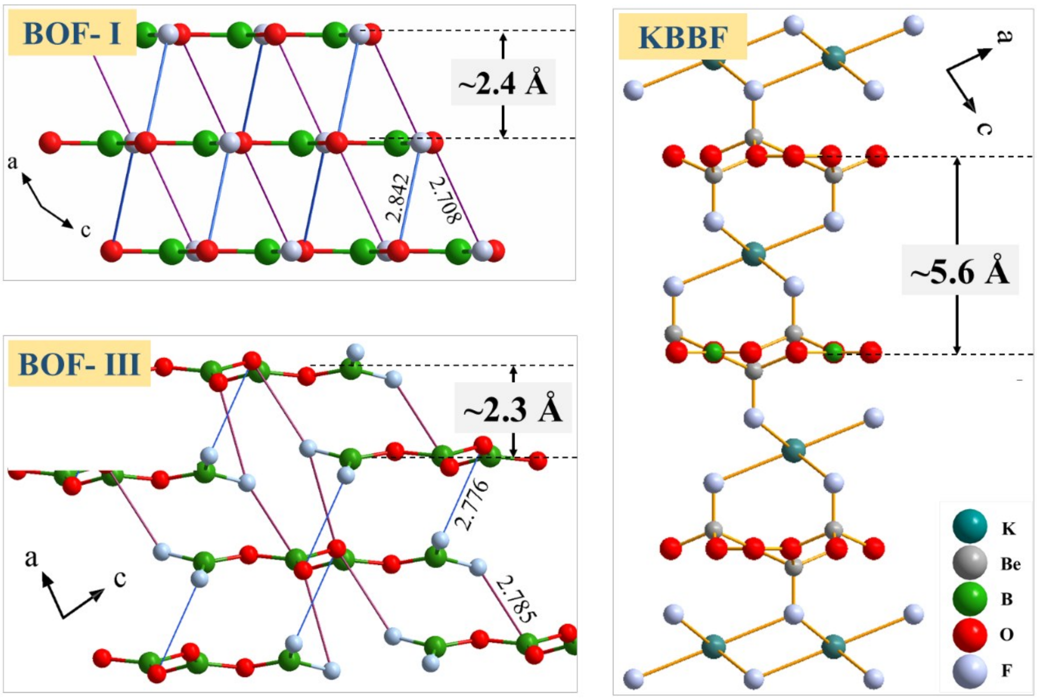


New covalent coordination pattern of F atom connected with the B atoms:

(1) terminal site F atoms (-B--F);

(2) bridging site F atoms (-B--F--B-).

Figure S4. The interlayer spacing of the structure Ⅰ, Ⅲ and $KBe_2BO_3F_2$ structure.



Predicted structure Ⅰ, Ⅲ with small interlayer space and B-F secondary bonds can effectively suppress the layering tendency.

Reference

[1] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, M. C. Payne, *Z. Kristallogr.* 2005, 220, 567–570.

[2] A. M. Rappe, K. M. Rabe, E. Kaxiras, J. D. Joannopoulos, *Phys. Rev. B* 1990, 41, 1227.

[3] J. Lin, A. Qteish, M. Payne, V. Heine, *Phys. Rev. B* 1993, 47, 4174.

[4] M.-H. Lee, *Ph.D. Thesis,* The University of Cambridge, 1996.

[5] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 1996, 77, 3865–3868.

[6] (a). W. Jia, J. Fu, Z. Cao, L. Wang, X. Chi, W. Gao, L. W. Wang, *J. Comp. Phys*. 2013.251, 102-115. (b). D.R. Hamann, Optimized norm-conserving Vanderbilt pseudopotentials, Phys. Rev. B 88 (2013) 0851171-10.

[7] C. J. Pickard, R. J. Needs, *J Phys- Condens Mater.* 2011, 23, 053201.

[8] A. O. Lyakhov, A. R. Oganov, H. T. Stokes, Q. Zhu, *Comput. Phys. Commun.* 2013, 184, 1172–1182.

[9] S. G. Jantz, F. Pielnhofer, L. van Wüllen, R. Weihrich, M. J. Schäfer, H. A. Höppe, *Chem. -Eur. J.* 2018, 24, 443– 450.