

## **New Antimony Fluorooxoborates with Great Birefringence and Unprecedented Structural Characterisation**

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## EXPERIMENTAL METHODOLOGY

### 1. Synthesis.

Crystals of  $\text{SbB}_2\text{O}_4\text{F}$  were obtained by a high-temperature solution method in a closed system. The raw materials  $\text{SbF}_3$ ,  $\text{B}_2\text{O}_3$ , and  $\text{H}_3\text{BO}_3$  at a molar ratio of 3:6:2 were placed in a fused-silica tube ( $\Phi 10 \text{ mm} \times 150 \text{ mm}$ ) and mixed in sealed quartz tubes under  $10^{-3} \text{ Pa}$  at a medium temperature of 653 K.

### 2. Characterizations.

High-quality crystals were picked under an optical microscope (OM) and applied for the measurements of single-crystal X-ray diffraction. The experiments were carried out at room temperature on a Bruker D8 Venture diffractometer with monochromatic Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The diffraction data were integrated using the SAINT program. Meanwhile, multiscan-type absorption corrections were performed using the SADABS program. To determine the space groups, the XPREP program in the SHELXTL package was used.<sup>[1]</sup> The crystal structure of  $\text{SbB}_2\text{O}_4\text{F}$  was solved by the direct method, and refined using  $F^2$  full matrix least squares. Then, the structure was checked by the PLATON program.<sup>[2-3]</sup> The bond valence sum (BVS) calculations were shown for verifying structural correctness.<sup>[4]</sup> Energy Dispersive X-ray Spectroscopy (EDS) was measured on a SUPRA 55VP field emission scanning electron microscope equipped with a BRUKER X-ray Flash-SDD-5010 energy-dispersive X-ray spectroscopy.

### 3. Calculations

The theoretical calculations of  $\text{SbB}_2\text{O}_4\text{F}$  are performed using the plane wave density functional theory (DFT) package CASTEP.<sup>[5, 6]</sup> The exchange-correlation functional was treated by the generalized gradient approximation (GGA) in the formulation of Perdew-Burke-Ernzerhoff (PBE) functional, and core-valence interactions were described by norm-conserving pseudopotentials (NCP).<sup>[7, 8]</sup> Because GGA usually underestimates the bandgap owing to the discontinuity of exchange-correlation energy, the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional<sup>[9]</sup> was chosen to provide more accurate band gap values. Therefore, the bandgap difference between the GGA and experimental value or HSE06 methods was used as the

operation of a scissor to calculate optical properties. The cutoff energy of the plane wave was set to 850 eV. Self-consistent field (SCF) calculations were performed with a convergence criterion of  $10^{-6}$  eV/atom on the total energy. The  $k$ -point separation for each material was set as  $0.07 \text{ \AA}^{-1}$  in the Brillouin zone, resulting in the corresponding Monkhorst-Pack  $k$ -point meshes. The linear optical properties were obtained based on the dielectric function:  $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ . Where  $\varepsilon_1(\omega)$  and  $\varepsilon_2(\omega)$  are the real and imaginary parts of the dielectric function respectively. The imaginary part of the dielectric function  $\varepsilon_2$  can be calculated based on the electronic structures and the real part is obtained by the Kramers-Kronig transformation, accordingly, the refractive indices and the birefringence ( $\Delta n$ ) can be calculated.

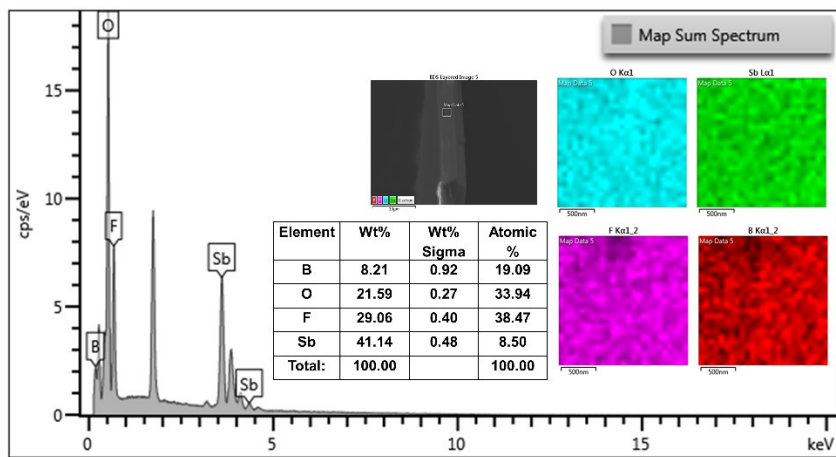


Fig. S1 EDS analysis of  $\text{SbB}_2\text{O}_4\text{F}$ .

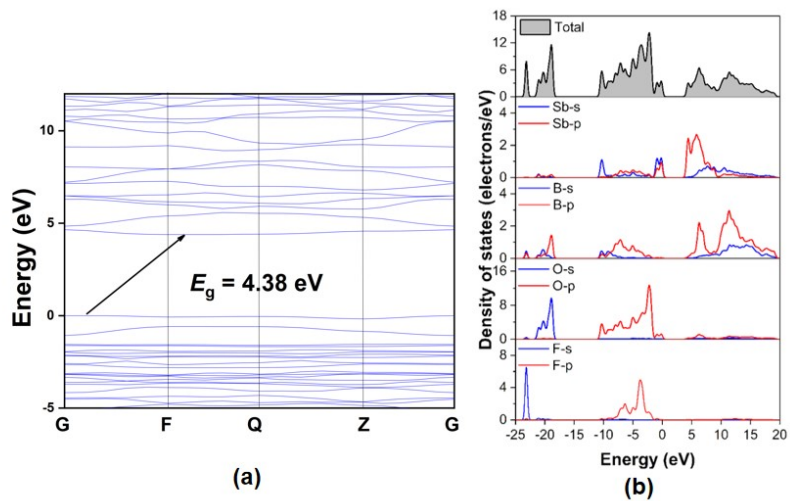


Fig. S2 The band structure(a) and density of states(b) of  $\text{SbB}_2\text{O}_4\text{F}$ .

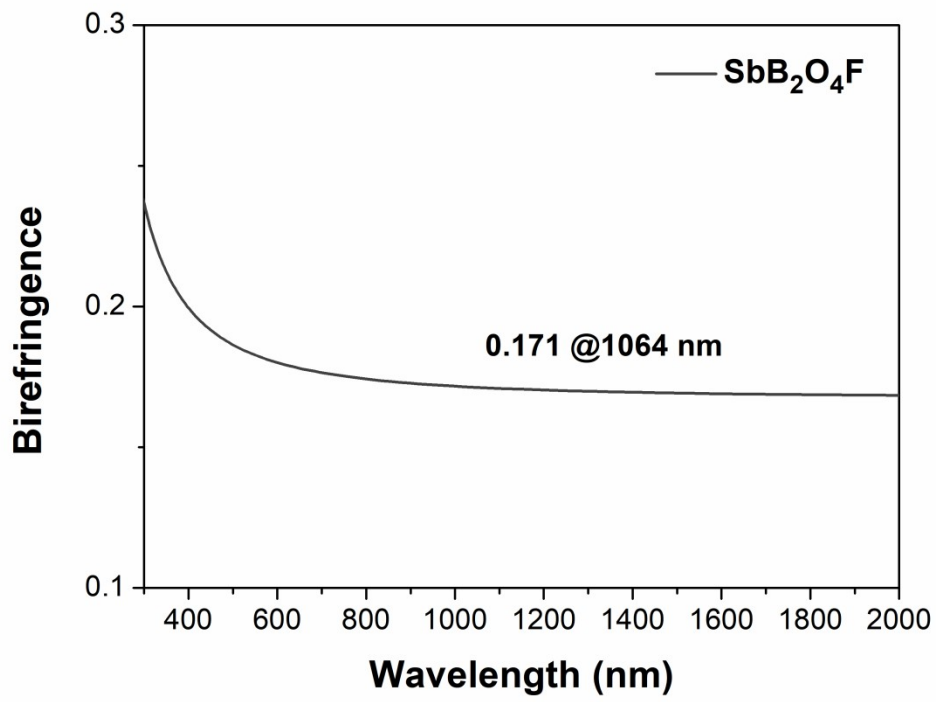


Fig. S3 The calculated birefringence of  $\text{SbB}_2\text{O}_4\text{F}$  crystal.

**Table S1.** Crystal data and structure refinements for SbB<sub>2</sub>O<sub>4</sub>F.

<b>Empirical formula</b>	<b>SbB<sub>2</sub>O<sub>4</sub>F</b>
<b>Temperature (K)</b>	300(2)
<b>Wavelength (Å)</b>	0.71073
<b>Crystal system</b>	triclinic
<b>Space group</b>	$P\bar{1}$
<b>Formula weight</b>	226.37
<b><i>a</i> (Å)</b>	4.3436(7)
<b><i>b</i> (Å)</b>	6.3169(10)
<b><i>c</i> (Å)</b>	7.0009(12)
<b><math>\alpha</math> (°)</b>	92.888(8)
<b><math>\beta</math> (°)</b>	95.126(7)
<b><math>\gamma</math> (°)</b>	104.803(7)
<b>Z, Volume (Å<sup>3</sup>)</b>	2, 184.44(5)
<b><math>\rho_{\text{Calcd}}</math> (g/m<sup>3</sup>)</b>	4.076
<b><math>\mu</math>(/mm)</b>	7.390
<b><i>F</i>(000)</b>	204.0
<b><i>R</i>(int)</b>	0.0919
<b>Goodness-of-fit on <i>F</i><sup>2</sup></b>	1.169
<b>Final <i>R</i> indices [<i>F</i><sub>o</sub><sup>2</sup>&gt;2<math>\sigma</math>(<i>F</i><sub>o</sub><sup>2</sup>)]<sup>a</sup></b>	<i>R</i> <sub>1</sub> = 0.0630, <i>wR</i> <sub>2</sub> = 0.1626
<b><i>R</i> indices (all data)<sup>a</sup></b>	<i>R</i> <sub>1</sub> = 0.0699, <i>wR</i> <sub>2</sub> = 0.1667
<b>Largest diff. peak and hole (e<sup>-</sup>Å<sup>-3</sup>)</b>	2.790/-1.827

<sup>[a]</sup>  $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$  and  $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$  for  $F_o^2 > 2\sigma(F_o^2)$ .

**Table S2.** Fractional atomic Coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for

$\text{SbB}_2\text{O}_4\text{F}$ .  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalised  $U_{ij}$  tensor.

<b>Atom</b>	<b>x</b>	<b>y</b>	<b>z</b>	<b><math>U(\text{eq})</math></b>	<b><math>BVS</math></b>
Sb(1)	3818(3)	5996(2)	2930(2)	18(1)	2.99
B(1)	10240(40)	-500(30)	2880(30)	10(4)	3.03
B(2)	6100(50)	1720(40)	2780(30)	17(4)	3.03
O(1)	9110(30)	1300(20)	2930(20)	25(3)	2.00
O(2)	5810(30)	3460(20)	4222(19)	16(3)	2.21
O(4)	3500(30)	9670(20)	2961(18)	16(3)	2.01
O(3)	8260(30)	7430(20)	2816(19)	23(3)	2.17
F(1)	5370(30)	2490(20)	955(16)	24(3)	0.67



**Table S3.** Bond lengths for SbB<sub>2</sub>O<sub>4</sub>F.

<b>Atom</b>	<b>Length/Å</b>
Sb(1)-O(2)	2.204(12)
Sb(1)-O(2)#1	1.991(13)
Sb(1)-O(3)	1.920(14)
Sb(1)-O(4)	2.362(13)
B(1)-O(1)	1.35(2)
B(1)-O(4)#2	1.39(2)
B(1)-O(3)#3	1.37(2)
B(2)#4-O(4)	1.50(2)
B(2)-O(1)	1.39(3)
B(2)-O(2)	1.49(2)
B(2)-F(1)	1.43(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 x+1,y-1,z #3 x,y-1,z  
#4 x,y+1,z #5 x-1,y+1,z

**Table S4.** Bond angles for SbB<sub>2</sub>O<sub>4</sub>F.

Atom	Angle/°
O(3)-Sb(1)-O(4)	80.9(5)
O(3)-Sb(1)-O(2)#1	92.7(5)
O(3)-Sb(1)-O(2)	82.6(5)
O(2)#1-Sb(1)-O(4)	83.5(5)
O(2)-Sb(1)-O(4)	149.7(5)
O(2)#1-Sb(1)-O(2)	72.0(5)
O(3)#3-B(1)-O(4)#2	116.9(16)
O(1)-B(1)-O(4)#2	121.1(17)
O(1)-B(1)-O(3)#3	122.0(16)
F(1)-B(2)-O(4)#3	106.4(15)
F(1)-B(2)-O(2)	104.9(16)
O(2)-B(2)-O(4)#3	108.6(14)
O(1)-B(2)-O(4)#3	111.3(17)
O(1)-B(2)-F(1)	111.3(15)
O(1)-B(2)-O(2)	113.8(16)

Symmetry transformations used to generate equivalent atoms:

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

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

**Table S5.** The optical properties of compounds with one-dimensional chains.

Compound	1D Chain Type	Anionic framework	$E_g$ (eV)	$\Delta n$
$\text{Li}_{0.5}\text{Na}_{0.5}\text{AlB}_2\text{O}_4\text{F}_2$	$\text{BO}_3$	$[\text{BO}_2]_\infty$	6.04	$\geq 0.110$
<i>Cc</i> -BaBOF <sub>3</sub>	$\text{BO}_2\text{F}_2$	$[\text{BOF}_2]_\infty$	6.42	0.020 <sup>a</sup>
$\text{BiB}_2\text{O}_4\text{F}$	$\text{BO}_4+\text{BO}_3\text{F}$	$[\text{B}_6\text{O}_{10}\text{F}_2]_\infty$	4.43	0.018 <sup>a</sup>
BaAsBO <sub>5</sub>	$\text{BO}_4$	$[\text{BO}_3]_\infty$	5.93	0.028
$\text{Li}_2\text{B}_3\text{O}_4\text{F}_3$	$\text{BO}_3+\text{BO}_3\text{F}+\text{BO}_2\text{F}_2$	$[\text{B}_3\text{O}_4\text{F}_3]_\infty$	8.43	0.050 <sup>a</sup>
$(\text{Pb}_4\text{O})\text{Pb}_2\text{B}_6\text{O}_{14}$	$\text{BO}_3+\text{BO}_4$	$[\text{B}_6\text{O}_{14}]_\infty$	2.98	0.054

<sup>a</sup> The first principles calculation result.

## REFERENCES

- (1) Sheldrick, G. M. A Short History of SHELX. *Acta Crystallogr. A* **2008**, 64, 112-122.
- (2) Haming, L.; Sheldrick, G. M. SADABS: A Program For Exploiting The Redundancy of Area-Detector X-Ray Data. *Acta Crystallogr. A* **1999**, 55, No. 206.
- (3) Spek, A. L. Single-Crystal Structure Validation with the Program PLATON. *J. Appl. Crystallogr.* **2003**, 36, 7-13.
- (4) Brese, N. E.; O'Keeffe, M. Bond-valence Parameters for Solids. *Acta Crystallogr., Sect. B: Struct. Sci.* **1991**, 47, 192-197.
- (5) Clark, S. J.; Segall, M. D.; Pickard, C. J.; Hasnip, P. J.; Probert, M. I.; Refson, K.; Payne, M. C. First Principles Methods Using CASTEP. *Z. Kristallogr. - Cryst. Mater.* **2005**, 220, 567.
- (6) Kohn, W. Nobel Lecture: Electronic Structure of Matterwave Functions and Density Functionals. *Rev. Mod. Phys.* **1999**, 71, 1253.
- (7) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865.
- (8) Rappe, A. M.; Rabe, K. M.; Kaxiras, E.; Joannopoulos, J. D. Optimized Pseudopotentials. *Phys. Rev. B* **1990**, 41, 1227.
- (9) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid Functionals Based on a Screened Coulomb Potential. *J. Chem. Phys.* **2003**, 118, 8207-8215.