Electronic Supplementary Information

An Antimony (III) Borate with Large Birefringence Exhibiting Unwonted $[B_5O_{11}]$ Fundamental Building Block and Dimeric $[Sb_2O_6]$ Cluster

Zhen Chen,[a,b,#] Hao Zeng,[a,#] Shujuan Han,[a,b]* Zhihua Yang,[a,b] and Shilie Pan [a,b]*

[a]CAS Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics & 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.

[#]These authors contributed equally to this work.

*Corresponding author, E-mail: slpan@ms.xjb.ac.cn

Table S1. Crystal data and structure refinement for SbB_5O_9.

Empirical formula	SbB_5O_9
Temperature	296.15 K
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions (Å)	a = 4.3535(4)
	b = 26.18(2) β=113.526(5)
	c = 6.6465(6)
Volume ($Å^3$)	694.57(11)
Z, Calculated density (g/cm^3)	4, 3.058
Absorption coefficient(mm^{-1})	4.000
F(000)	592
Theta range for data collection(°)	3.113 - 25.242
Limiting indices	$-5 \le h \le 5$, $-31 \le k \le 34$, $-8 \le l \le 8$
Reflections collected / unique	8877 / 1597 [R(int) = 0.0556]
Completeness to theta	99.90%
Goodness-of-fit on F^2	1.110
Final R indices [$F_o^2 > 2\sigma(F_c^2)$][a]	R_1 = 0.0244, wR_2 = 0.0495
R indices (all data)[a]	R_1 = 0.0319, wR_2 = 0.0513
Largest diff. peak and hole ($e \cdot Å^{-3}$)	0.553 and - 0.733

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

Table S2. Atomic coordinates (× 10^4), equivalent isotropic displacement parameters (Å^2 × 10^3) and bond valence sum (BVS) calculations for SbB_5O_9. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	*U*(eq)	BVS
Sb(1)	-1867(1)	-559(1)	13937(1)	8(1)	2.83
B(1)	854(11)	-564(2)	10315(7)	8(1)	3.04
B(2)	4533(10)	-577(2)	8146(6)	9(1)	3.07
B(3)	4668(12)	-1530(2)	7579(7)	12(1)	3.04
B(4)	9185(12)	-2086(2)	9577(8)	16(1)	3.06
B(5)	4098(12)	-2430(2)	6998(8)	15(1)	3.07
O(1)	1110(7)	-634(1)	12400(4)	12(1)	2.09
O(2)	3970(6)	-548(1)	10179(4)	9(1)	1.99
O(3)	-1997(6)	-492(1)	8523(4)	10(1)	1.88
O(4)	2395(6)	-209(1)	6453(4)	8(1)	2.21
O(5)	3276(7)	-1069(1)	7054(4)	11(1)	1.87
O(6)	7862(7)	-1604(1)	9116(5)	18(1)	2.00
O(7)	12377(7)	-2141(1)	11031(5)	20(1)	2.09
O(8)	2764(7)	-1951(1)	6493(4)	18(1)	1.95
O(9)	7279(7)	-2499(1)	8513(5)	22(1)	2.02

Table S3. Selected bond lengths (Å) and angles (°) for SbB_5O_9.

Sb(1)-O(1)	1.954(2)	B(2)- O(5)	1.472(5)
Sb(1)-O(2)#2	2.431(2)	B(3)-O(5)	1.333(5)
Sb(1)-O(4)#3	2.030(2)	B(3)-O(6)	1.372(5)
Sb(1)-O(4)#4	2.145(2)	B(3)-O(8)	1.396(5)
B(1)-O(1)	1.358(4)	B(4)-O(6)	1.370(5)
B(1)-O(2)	1.396(5)	B(4)-O(7)	1.347(5)
B(1)-O(3)	1.347(5)	B(4)-O(9)	1.374(5)
B(2)-O(2)	1.468(4)	B(5)#5-O(7)	1.361(5)
B(2)#2-O(3)	1.446(5)	B(5)-O(8)	1.365(5)
B(2)-O(4)	1.491(5)	B(5)-O(9)	1.360(5)
O(1)-Sb(1)-O(2)#2	80.93(10)	O(3)#6-B(2)-O(4)	109.0(3)
O(1)-Sb(1)-O(4)#3	95.56(10)	O(3)#6-B(2)-O(5)	112.1(3)
O(1)-Sb(1)-O(4)#4	84.39(10)	O(5)-B(2)-O(4)	101.3(3)
O(4)#3-Sb(1)-O(2)#2	81.77(9)	O(5)-B(3)-O(6)	122.9(4)
O(4)#4-Sb(1)-O(2)#2	148.61(8)	O(5)-B(3)-O(8)	117.8(4)
O(4)#3-Sb(1)-O(4)#4	72.20(11)	O(6)-B(3)-O(8)	119.3(3)
O(1)-B(1)-O(2)	112.6(3)	O(6)-B(4)-O(9)	119.7(4)
O(2)-B(2)-O(4)	112.2(3)	O(7)-B(4)-O(6)	118.7(4)
O(2)-B(2)-O(5)	109.4(3)	O(7)-B(4)-O(9)	121.6(4)
O(3)-B(1)-O(1)	126.3(3)	O(7)#8-B(5)-O(8)	122.8(4)
O(3)-B(1)-O(2)	121.0(3)	O(9)-B(5)-O(7)#8	116.4(3)
O(3)#6-B(2)-O(2)	112.3(3)	O(9)-B(5)-O(8)	120.8(4)

Symmetry transformations used to generate equivalent atoms:

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

#4 x,y,z+1 #5 x+1,-y-1/2,z+1/2 #6 x+1,y,z

#7 x,y,z-1 #8 x-1,-y-1/2,z-1/2

Table S4. The antimony borates.

	Formula	Space group	Band gap (eV)		Sb-O framework	Ref.
			Cal.	*Exp.*		
Sb Ⅲ	SbB_5O_9*	$P2_1/c$	4.10	4.66	Dimeric $[Sb_2O_6]$ cluster	
	SbB_3O_6	Cc	4.08	3.95	Isolated SbO_4	1
Sb Ⅴ	$Na_2SbB_3O_8$	$P2_1/c$	4.22	3.89	Isolated SbO_6	2
	$K_2SbB_3O_8$	$P2_1/c$	4.18	3.69	Isolated SbO_6	2
	$Rb_2SbB_3O_8$	$P2_1/c$	4.21	4.82	Isolated SbO_6	2
	$KSbB_2O_6$	Cc	3.61	3.63	Corner-sharing SbO_6	3
	$BaSb_2B_4O_{12}$	$C2/c$	3.94	4.26	Corner-sharing SbO_6	3
	$SmSb_2BO_8$	$Pnma$	/	3.54	Corner-sharing SbO_6	4
	$EuSb_2BO_8$	$Pnma$	/	3.46	Corner-sharing SbO_6	4
	$GdSb_2BO_8$	$Pnma$	/	3.48	Corner-sharing SbO_6	4
	$TbSb_2BO_8$	$Pnma$	/	3.53	Corner-sharing SbO_6	4
	β-$RbSbB_2O_6$	Cc	3.639	/	Corner-sharing SbO_6	2
	$K_3Sb_4BO_{13}$	$P\bar{1}$	/	/	Corner-sharing SbO_6	5

* represents the work

Note: the above compounds are all derived from the Inorganic Crystal Structure Database (ICSD), and the antimony inorganic borates except for disorder and obvious errors are listed in the statistical data.

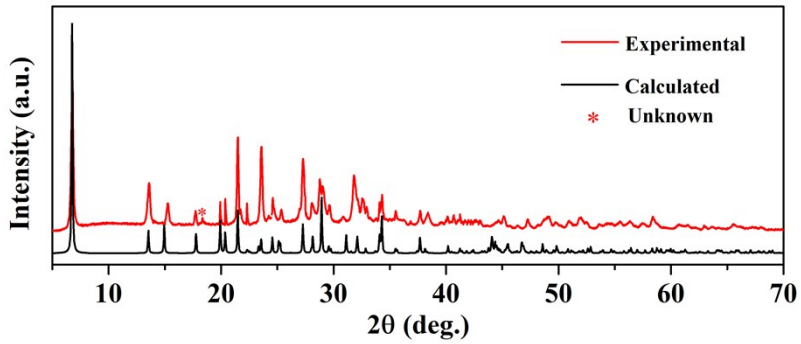

Figure S1. Experimental and calculated XRD patterns of SbB_5O_9.

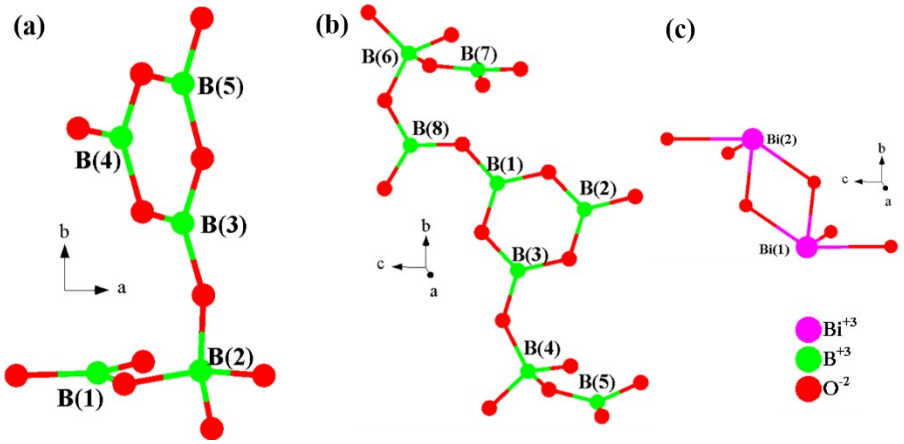

Figure S2. The fundamental building block (a) $[B_5O_{11}]$ of SbB_5O_9 and (b) $[B_8O_{18}]$ of $Bi_2B_8O_{15}$; (c) The $[Bi_2O_6]$ dimeric cluster.

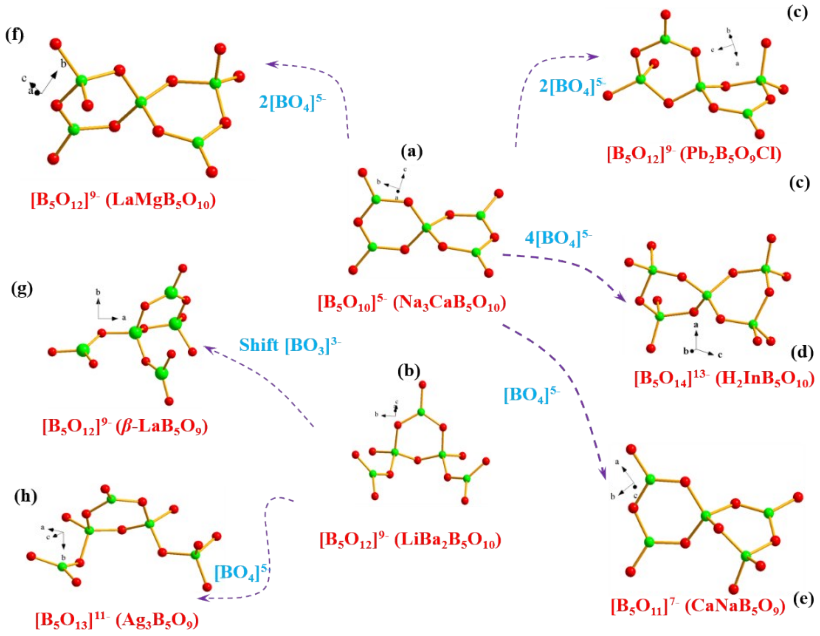

Figure S3. The fundamental building blocks $[B_5O_n]$ (n= 10, 11, 12, 13, 14) from different borates.

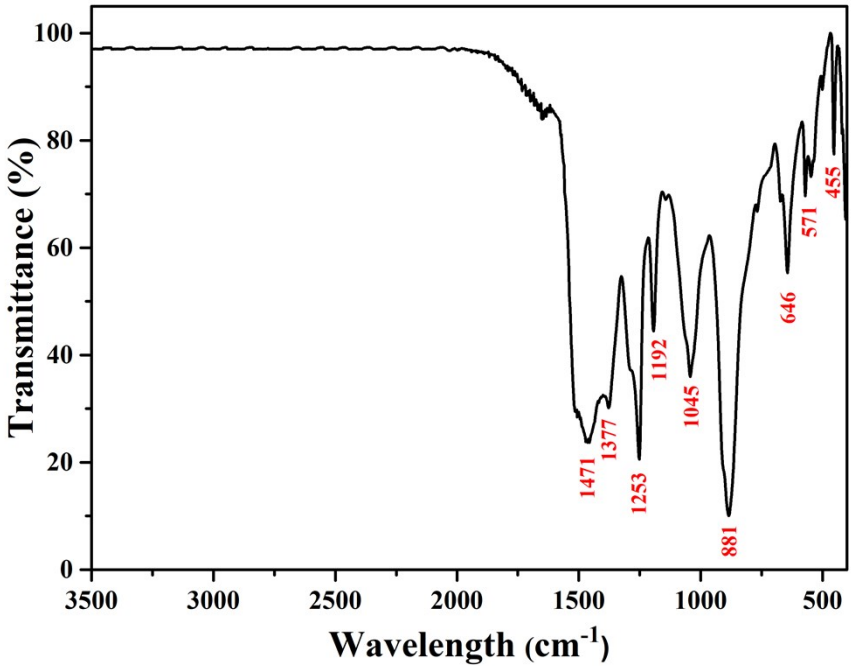

Figure S4. The IR spectrum of SbB_5O_9.

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