Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Synthesis, characterization and theoretical studies of the nonlinear optical crystal $Sr_2B_5O_9(OH)·H_2O$

Fangyuan Zhang,[a,b] Fangfang Zhang,*[b] Qun Jing,[b] Shilie Pan,*[b] Zhihua Yang[b] and Dianzeng Jia[a]

[a] College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China

[b] Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Xinjiang Key Laboratory of Electronic Information Materials and Devices, Urumqi 830011, China.

*Corresponding authors, E-mails: ffzhang@ms.xjb.ac.cn, slpan@ms.xjb.ac.cn

Single crystal X-ray diffraction measurement

Single crystal X-ray diffraction data were collected at RT on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å). The data were integrated using the SAINT program, and numerical absorption corrections were performed using the SADABS program.[1] The structure was solved by direct method and refined with a full-matrix least-squares technique using programs from the SHELXTL crystallographic software package.[2] Anisotropic thermal parameters were applied to all nonhydrogen atoms. Hydrogen atoms were placed in geometrically idealized positions. The structure was verified using the *Addsym* subroutine of PLATON[3] and no higher symmetries were found.

Table S1. Crystal data and structural refinement for $Sr_2B_5O_9(OH)\cdot H_2O$ at 297K

formula	$Sr_2B_5O_9(OH)\cdot H_2O$
fw /g·mol^{-1}	408.31
crystal system	monoclinic
space group	*C*2 (No. 5)
a / Å	10.2342(15)
b / Å	8.0240(13)
c / Å	6.3898(9)
β / deg	127.882(7)
V / Å^3	414.15(11)
Z	2
ρ_{calcd} / g·cm^{-3}	3.274
μ / mm^{-1}	12.938
F(000)	384
crystal size / mm^3	0.146 × 0.110 × 0.085
θ_{max} / deg	27.45
reflections collected / unique	2374 / 867
R (int)	0.0246
completeness	100 %
GOF on F^2	0.940
R_1, wR_2 (I>2σ(I)) [a]	0.0174, 0.0392
R_1, wR_2 (all data)	0.0183, 0.0395
flack parameter	0.006(9)

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

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Sr_2B_5O_9(OH)\cdot H_2O$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyckoff positions	*x/a*	*y/b*	*z/c*	U_{eq}	BVS
Sr1	4*c*	7046(1)	5352(1)	9147(1)	10(1)	2.1
B1	4*c*	9257(5)	2504(6)	7442(7)	9(1)	3.0
B2	2*b*	5000	9164(7)	5000	8(1)	3.0
B3	4*c*	7666(5)	5038(6)	5073(8)	10(1)	3.0
O1	4*c*	6466(3)	6092(3)	4532(5)	9(1)	2.1
O2	4*c*	7991(3)	3748(3)	6753(5)	9(1)	2.0
O3	2*a*	5000	6713(4)	10000	8(1)	2.0
O4	4*c*	5673(3)	2611(4)	8933(6)	18(1)	0.6[a]
O5	4*c*	5531(3)	8245(3)	7358(5)	7(1)	2.1
O6	4*c*	8559(2)	5262(5)	14149(4)	10(1)	2.0

[a] bond valence sum of O4 without hydrogen coordinates.

Table S3 Selected bond lengths (Å) and bond angles (deg.) for $Sr_2B_5O_9(OH)\cdot H_2O$ [a]

Sr1–O6	2.555(2)	$O3^{\#7}$–B1–$O5^{\#7}$	111.0(3)
Sr1–O4	2.563(3)	$O3^{\#7}$–B1–O2	112.9(3)
Sr1–O2	2.598(3)	$O5^{\#7}$–B1–O2	110.4(4)
Sr1–$O4^{\#1}$	2.599(3)	$O3^{\#7}$–B1–$O1^{\#8}$	105.2(4)
Sr1–O5	2.635(3)	$O5^{\#7}$–B1–$O1^{\#8}$	105.2(3)
Sr1–$O5^{\#2}$	2.684(3)	O2–B1–$O1^{\#8}$	111.7(3)
Sr1–O1	2.697(3)	$O5^{\#3}$–B2–O5	119.0(5)
Sr1–O3	2.6971(16)	$O5^{\#3}$–B2–$O6^{\#1}$	109.45(14)
Sr1–$O1^{\#3}$	2.900(3)	O5–B2–$O6^{\#1}$	105.40(15)
B1–$O3^{\#7}$	1.453(5)	$O5^{\#3}$–B2–$O6^{\#9}$	105.40(15)
B1–$O5^{\#7}$	1.466(5)	O5–B2–$O6^{\#9}$	109.45(14)
B1–O2	1.471(5)	$O6^{\#1}$–B2–$O6^{\#9}$	107.7(5)
B1–$O1^{\#8}$	1.507(5)	O1–B3–$O6^{\#10}$	123.2(5)
B2–$O5^{\#3}$	1.446(4)	O1–B3–O2	114.6(3)
B2–O5	1.446(4)	$O6^{\#10}$–B3–O2	122.1(4)
B2–$O6^{\#1}$	1.508(5)		
B2–$O6^{\#9}$	1.508(5)		
B3–O1	1.350(6)		
B3–$O6^{\#10}$	1.371(4)		
B3–O2	1.383(6)		
Geometrically estimated hydrogen bonds			
$O4^{\#6}\cdots H1^{\#5}$	1.2401(40)	$O4^{\#6}$–$H1^{\#5}$–$O4^{\#7}$	179.778(216)
$O4^{\#6}\cdots O4^{\#7}$	2.4801(56)		
$O4^{\#6}\cdots H2^{\#10}$	0.8785(23)	$O4^{\#6}$–$H2^{\#10}$–$O6^{\#11}$	179.547(169)
$O4^{\#6}\cdots O6^{\#11}$	3.0697(36)		
Numerical refined hydrogen Bonds			
$O4^{\#6}\cdots H1^{\#5}$	1.2219	$O4^{\#6}$–$H1^{\#5}$–$O4^{\#7}$	179.155
$O4^{\#6}\cdots O4^{\#7}$	2.4437		
$O4^{\#6}\cdots H2^{\#10}$	0.9716	$O4^{\#6}$–$H2^{\#10}$–$O6^{\#11}$	150.653
$O4^{\#6}\cdots O6^{\#11}$	3.1172		

[a] Symmetry transformations used to generate equivalent atoms:

#1 –x+3/2, y+1/2, –z+2; #2 –x+3/2, y–1/2, –z+2; #3 –x+1, y, –z+1; #4 x–1/2, y+1/2, z; #5 x+1/2, y–1/2, z+1; #6 x, y, z+1; #7 x+1/2, y–1/2, z; #8 –x+3/2, y–1/2, –z+1; #9 x–1/2, y+1/2, z–1; #10 x, y, z–1; #11 –x+3/2, y+1/2, –z+1; #12 –x+1, y, –z+2

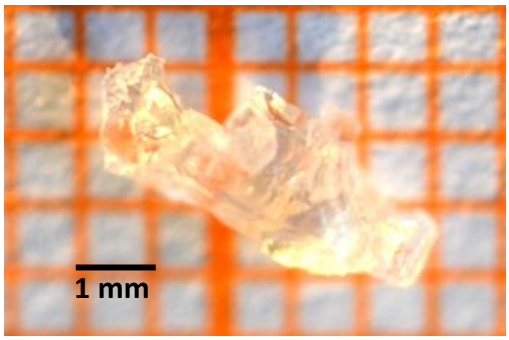

Fig. S1 Photograph of the $Sr_2B_5O_9(OH)\cdot H_2O$ crystal.

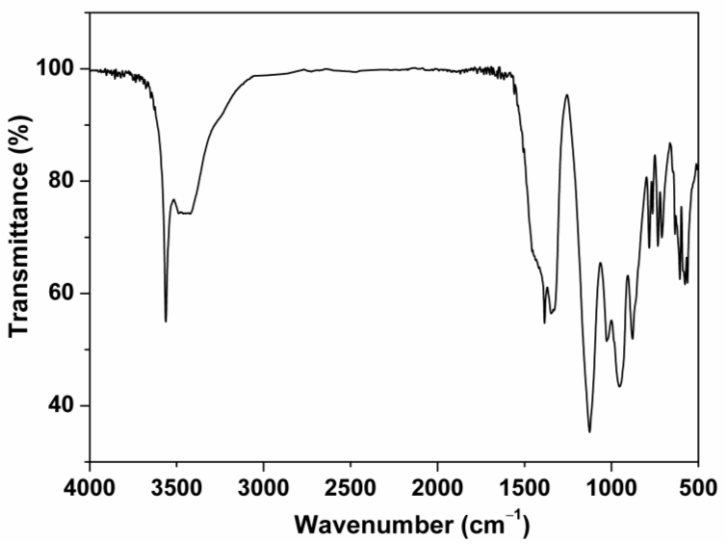

Fig. S2. IR spectrum of $Sr_2B_5O_9(OH)\cdot H_2O$.

The Mulliken analysis and electron densities

The chemical bond character can be clearly identified by Mulliken analysis[4] and electron density calculation, which, according to the reviewer' comment, have been carried out. Results have shown that Mulliken overlap populations of B-O and O-H bonds are 0.56 ~ 0.78 and 0.35 ~ 0.59, respectively, whereas those for Sr-O bonds are much smaller, i.e., 0.04 ~ 0.10. It indicates the covalency of the B-O and O-H bonds and iconicity of the Sr-O bonds, respectively. The chemical bond characters were further confirmed by electron densities of atoms which clearly show that the spherical electron distribution was found at strontium atoms, while the two-atom-sharing electron distribution was found in B-O bond and O-H bond (Fig. S3).

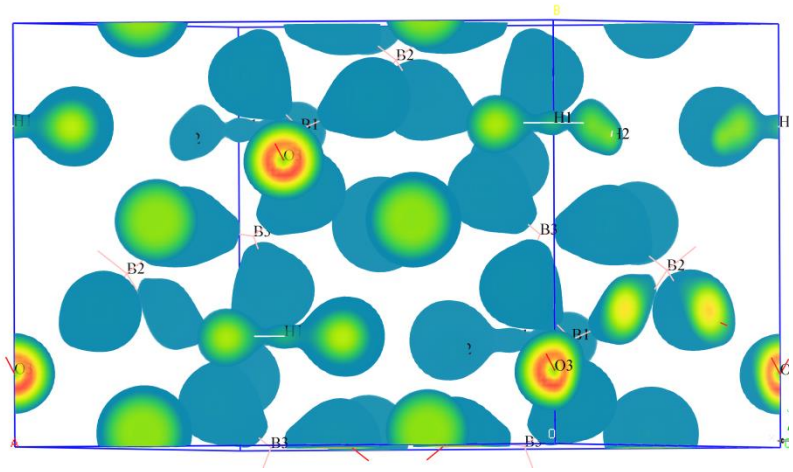

Fig. S3. Electron desity of atoms in $Sr_2B_5O_9(OH)\cdot H_2O$.

References

1. SAINT, Version 7.60A, Bruker Analytical X-ray Instruments, Inc., Madison, WI, 2008.

2. G. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112-122.

3. A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.

4. M. D. Segall, R. Shah, C. J. Pickard and M. C. Payne, *Phys. Rev. B* 1996, **54**, 16317-16320.