Supporting Information

$Ba_2B_5O_8(OH)_2(NO_3)\cdot 3H_2O$: the synthesis of an alkaline earth borate-nitrate optimized from a hydroxylic borate

Huaiyu Hu,[a,b] Junben Huang,[a] Zhiyong Guo,[c] Min Zhang,*[, a,b] Zhihua Yang,[a,b] 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. E-mail: zhangmin@ms.xjb.ac.cn（M. Zhang）, slpan@ms.xjb.ac.cn (S. L. Pan)

b. Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.

c. Xuchang Quality and Technical Supervision, Inspection and Testing Center, National Quality Supervision and Inspection Center for Ceramic Products of China, West Section of Longxing Road, Dongcheng District, Xuchang, Henan

Table S1. The final atomic coordinates and equivalent isotropic displacement parameters for $Ba_2B_5O_8(OH)_2(NO_3)\cdot 3H_2O$, U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, and the Bond Valence Sum for each atom in the asymmetric unit.

Atom	*x*	*y*	*z*	**U(eq)**	**BVS**
Ba1	0.95251(8)	0.28847(2)	0.93260(6)	0.01464(16)	2.22
Ba2	0.54796(9)	0.45620(2)	0.74455(6)	0.01891(17)	2.07
B1	0.0652(14)	0.3674(4)	0.5984(11)	0.0138(18)	3.02
B2	0.7834(16)	0.4332(5)	0.4549(11)	0.0160(19)	3.12
B3	0.4005(14)	0.3075(4)	0.6975(11)	0.0123(18)	3.01
B4	0.7003(14)	0.3309(4)	0.5705(10)	0.0112(17)	2.98
B5	0.4423(15)	0.2476(4)	0.9592(11)	0.0133(18)	3.03
N1	1.1519(15)	0.4465(4)	1.0110(12)	0.034(2)	4.99
O1	-0.0002(9)	0.4199(3)	0.5238(8)	0.0204(14)	1.79
O2	0.9793(12)	0.1829(3)	0.7564(8)	0.0265(15)	1.94
O3	-0.0707(9)	0.3228(2)	0.6177(7)	0.0121(11)	2.08
O4	0.6459(9)	0.3897(3)	0.5006(7)	0.0150(12)	1.88
O5	0.2741(8)	0.3620(3)	0.6499(7)	0.0143(12)	2.00
O6	0.6168(9)	0.3237(3)	0.7118(6)	0.0129(12)	1.99
O7	0.3395(9)	0.2402(3)	1.0778(7)	0.0137(12)	1.96
O8	0.3529(8)	0.2870(3)	0.8460(6)	0.0122(12)	1.96
O9	0.7277(10)	0.4921(3)	0.5094(8)	0.0209(14)	2.06
O10	0.6245(9)	0.2189(3)	0.9581(7)	0.0140(12)	2.03
O11	0.6379(11)	0.3759(3)	1.0085(8)	0.0279(16)	1.93
O12	1.3045(13)	0.4703(4)	0.9758(9)	0.0389(19)	2.07
O13	0.7552(12)	0.4339(4)	0.2836(8)	0.0292(16)	1.53
O14	0.6489(15)	0.6446(4)	0.7659(11)	0.047(2)	2.45
O15	1.1043(14)	0.4627(4)	1.1384(9)	0.043(2)	1.70
O16	1.0463(16)	0.4103(4)	0.9245(10)	0.050(2)	2.03

Table S2. Bond lengths (Å) and angles (°) for $Ba_2B_5O_8(OH)_2(NO_3)\cdot 3H_2O$

Ba1-O3#1	2.842(6)	Ba2-O4	2.788(6)
Ba1-O3#2	2.974(6)	Ba2-O5	2.780(6)
Ba1-O6	2.747(6)	Ba2-O6	2.994(6)
Ba1-O7#1	2.831(6)	Ba2-O9#4	2.818(6)
Ba1-O8#1	2.913(5)	Ba2-O9	2.712(7)
Ba1-O2	2.832(7)	Ba2-O11	2.886(7)
Ba1-O2#3	2.884(7)	Ba2-O12#5	2.941(8)
Ba1-O10	2.716(6)	Ba2-O12#6	2.864(7)
Ba1-O11	3.023(7)	Ba2-O13#4	3.136(8)
Ba1-O16	2.774(8)	Ba2-O15#5	2.939(9)
B1-O3	1.374(10)	B3-O5	1.481(11)
B1-O5	1.372(11)	B3-O6	1.460(11)
B1-O1	1.360(11)	B3-O8	1.476(10)
B2-O4	1.441(11)	B3#3-O7	1.487(11)
B2-O9	1.465(12)	B4-O4	1.452(10)
B2-O13	1.478(12)	B4-O6	1.470(10)
B2#6-O1	1.469(12)	B4-O3#1	1.502(10)
B5-O7	1.368(11)	B4-O10#8	1.497(11)
B5-O8	1.364(11)	B4#6-O3	1.502(11)
B5-O10	1.368(11)	B4#3-O10	1.497(11)
N1-O12	1.237(12)	N1-O15	1.276(12)
N1-O16	1.222(12)	O5-B1-O3	122.8(8)
O1-B1-O3	121.5(8)	O1-B1-O5	115.7(7)
O4-B2-O9	106.8(7)	O4-B2-O1#1	111.9(7)
O4-B2-O13	109.7(8)	O9-B2-O1#1	109.6(8)
O9-B2-O13	109.6(7)	O1#1-B2-O13	109.1(7)
O5-B3-O7#8	108.9(7)	O6-B3-O5	108.2(7)
O6-B3-O7#8	110.8(7)	O6-B3-O8	112.8(7)
O8-B3-O5	106.7(7)	O8-B3-O7#8	109.3(7)
O4-B4-O3#1	111.9(7)	O4-B4-O6	110.5(7)
O4-B4-O10#8	111.2(7)	O6-B4-O3#1	106.9(6)
O6-B4-O10#8	110.0(7)	O10#8-B4-O3#1	106.0(6)
O8-B5-O7	114.9(8)	O8-B5-O10	123.0(8)
O10-B5-O7	122.1(8)	O12-N1-O15	117.7(9)
O16-N1-O12	121.3(10)	O16-N1-O15	121.0(10)

Symmetry transformations used to generate equivalent atoms:

#1 1+x,+y,+z; #2 1+x,1/2-y,1/2+z; #3 +x,1/2-y,1/2+z; #4 1-x,1-y,1-z; #5 2-x,1-y,2-z; #6 -1+x,+y,+z; #7 -1+x,1/2-y,-1/2+z; #8 +x,1/2-y,-1/2+z

Table S3. crystal data and structure refinement for $Ba_2B_5O_8(OH)_2(NO_3)\cdot 3H_2O$ and $Ba_2B_5O_8(OH)_2OH$

Empirical formula	$Ba_2B_5O_8(OH)_2(NO_3)\cdot 3H_2O$	$Ba_2B_5O_8(OH)_2OH$[b]
Formula weight	606.80	507.7480
Temperature	301.0	Room temperature
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 6.6406(6),	a = 6.713(2),
	b = 22.157(2) Å, β = 101.980(4)°	b =16.480(5)Å,β = 106.80(3)°
	c = 8.7863(6),	c = 8.387(3),
Volume	1264.60(19) $Å^3$	888.3(5) $Å^3$
Z, Calculated density	4, 3.187 $g\cdot cm^{-3}$	4,3.80 $g\cdot cm^{-3}$
Absorption coefficient	6.287 mm^{-1}	/
$F(000)$	1120.0	/
Theta range for data collection	1.84 to 27.51°	/
Limiting indices	$-8 \le h \le 8$, $-25 \le k \le 28$, $-11 \le l \le 11$	/
Reflections collected / unique	12257 / 2904[R(int) = 0.0818]	/
Completeness	99.6%	/
Data / restraints / parameters	2904/11/232	/
Goodness-of-fit on F^2	1.079	/
Final R indices [$Fo^2 > 2\sigma(Fo^2)$][a]	R_1 = 0.0398, wR_2 = 0.0899	/
R indices (all data)[a]	R1 = 0.0502, wR2 = 0.1012	/
Largest diff. peak and hole	1.46 and -1.33e·$Å^{-3}$	/

[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 $F_o^2 > 2\sigma(F_o^2)$

[b]O. Ferro, S. Merlino, S. A. Vinogradova, D. Y. Pushcharovsky and O. V. Dimitrova, *J. Alloys Compd.*, 2000, **305**, 63-71.

Table S4. All of the borate-nitrates up till now

Type of the element	The formula of the compound	B-O anion framework	ICSD No. or reference
Alkali metal	$K_3Na[B_6O_9(OH)_3]NO_3$	Isolated $[B_6O_9(OH)_3]^{3-}$	427967
	$Na_3(NO_3)[B_6O_{10}]$	$^3_\infty[B_6O_{10}]^{2-}$	97687
	$Na_{3-x}K_x[B_6O_{10}]NO_3$ (x = 0.5, 0.6, 0.7)	$^3_\infty[B_6O_{10}]^{2-}$	432294-432296
	$M_3B_6O_{10}(NO_3)$(M=K,Rb)	$^3_\infty[B_6O_{10}]^{2-}$	[a]
	$Cs_3B_8O_{13}NO_3$	$^3_\infty[B_8O_{13}]^{2-}$	[b]
Lanthanide series metals	$Ce[B_5O_8(OH)(H_2O)]NO_3\cdot H_2O$	$^2_\infty[B_5O_8(OH)(H_2O)]^{2-}$	262731
	$La[B_5O_8(OH)]NO_3\cdot 2H_2O$	$^2_\infty[B_5O_8(OH)]^{2-}$	426014
	$La[B_5O_8(OH)H_2O]NO_3\cdot 2H_2O$	$^2_\infty[B_5O_8(OH)(H_2O)]^{2-}$	[c]
	$Lu_2B_2O_5(NO_3)_2\cdot 2H_2O$	Isolated $[B_2O_5]^{4-}$	430158
	$Pr[B_5O_8(OH)(H_2O)_{0.87}]NO_3\cdot 2H_2O$	$^2_\infty[B_5O_8(OH)(H_2O)_{0.87}]^{2-}$	433274
	$RE[B_5O_8(OH)(H_2O)_x]NO_3\cdot 2H_2O$ [RE = Nd (x = 0.85), Sm (x = 0)]	$^2_\infty[B_5O_8(OH)(H_2O)_x]^{2-}$	431164
Np	$K_2[(NpO_2)_3B_{10}O_{16}(OH)_2(NO_3)_2]$	$^2_\infty[B_5O_8(OH)]^{2-}$	168519
Pb	$[Pb_6(\mu_4\text{-}O)_4(BO_3)](NO_3)$	Isolated $[BO_3]^{3-}$	[d]
	$H[Pb_6(\mu_3\text{-}O)_2(BO_3)_2](NO_3)_3$	Isolated $[BO_3]^{3-}$	[d]
	$H[Pb_8(\mu_4\text{-}O)_3(\mu_3\text{-}O)(BO_3)_2](NO_3)_3$	Isolated $[BO_3]^{3-}$	[d]
	$Pb_2(BO_3)(NO_3)$	Isolated $[BO_3]^{3-}$	428943
	$[Pb_3(B_3O_7)](NO_3)$	Isolated $[B_3O_7]^{5-}$	250750
Co,Ni,Cu,Zn,Cd	$M_3B_7O_{13}(NO_3)$	$^3_\infty[B_7O_{13}]^{5-}$	[e]
	$K_7Ni[B_{18}O_{24}(OH)_9](NO_3)_6\cdot(H_3BO_3)$	Isolated $[B_{18}O_{24}(OH)_9]^{3-}$ And H_3BO_3	766
	$Cd_3[B_6O_9(OH)_2]_2.2NO_3\cdot 4H_2O$	$^2_\infty[B_6O_9(OH)_2]^{2-}$	18367

[a] Q. Q. Zhang, F. F. Zhang, F. M. Li, S. J. Han, Z. H. Yang and S. L. Pan, *Eur. J. Inorg. Chem*., **2021**, 1297-1304

[b] Z. L. Chen, C. F. Wu, H. Zeng and F. Yu, *Dalton Trans*., 2021, **50**, 8676-8679.

[c] L. Y. Li, G. B. Li, F. H. Liao and J. H. Lin, *Acta Phys. -Chim. Sin.*, 2005, **21**, 769-773.

[d] J. L. Song, X. Xu, C. L. Hu, F. Kong and J. G. Mao, *CrystEngComm*, 2015, **17**, 3953-3960.

[e] T. A. Bither and H. S. Young, *J. Solid State Chem.*, 1974, **10**, 302-311.

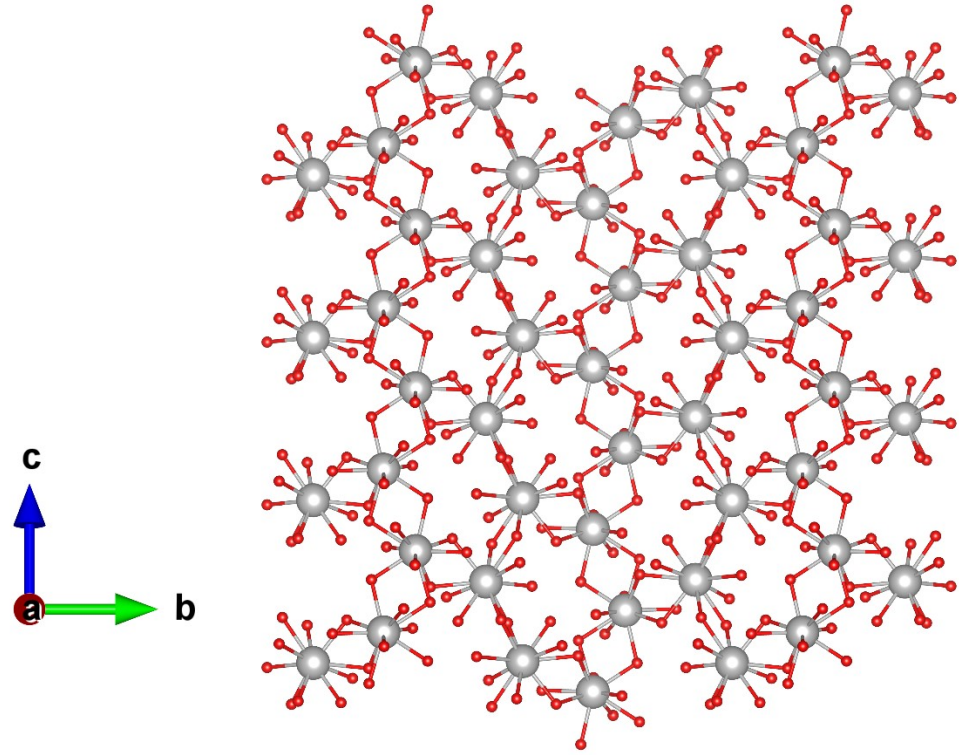

Figure S1. The Ba-O layer of $Ba_2B_5O_8(OH)_2(NO_3)\cdot 3H_2O$

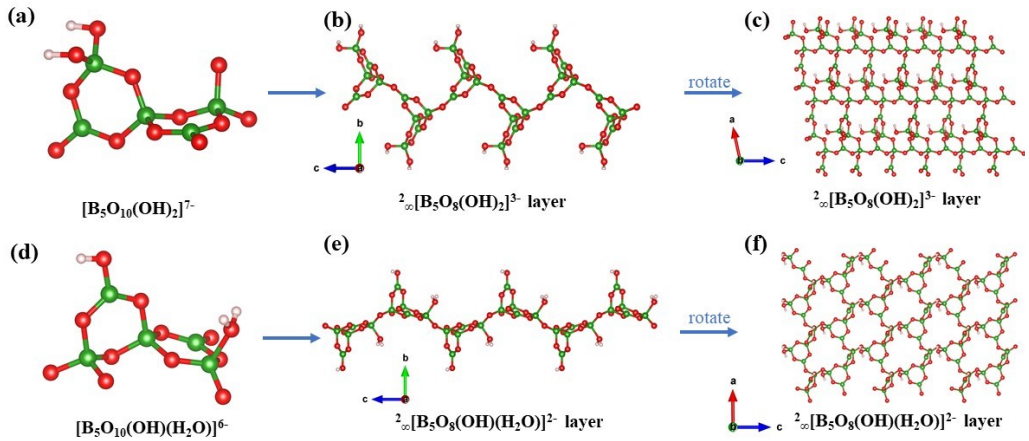

Figure S2. The B-O anions of $Ba_2B_5O_8(OH)_2(NO_3)\cdot 3H_2O$ and $Ce[B_5O_8(OH)(H_2O)]NO_3\cdot H_2O$. (a)(d) the fundamental basic units, (b)(c) the $^2_\infty[B_5O_8(OH)_2]^{3-}$ layer and (e)(f) the $^2_\infty[B_5O_8(OH)(H_2O)]^{2-}$ layer of $Ba_2B_5O_8(OH)_2(NO_3)\cdot 3H_2O$ and $Ce[B_5O_8(OH)(H_2O)]NO_3\cdot H_2O$, respectively.

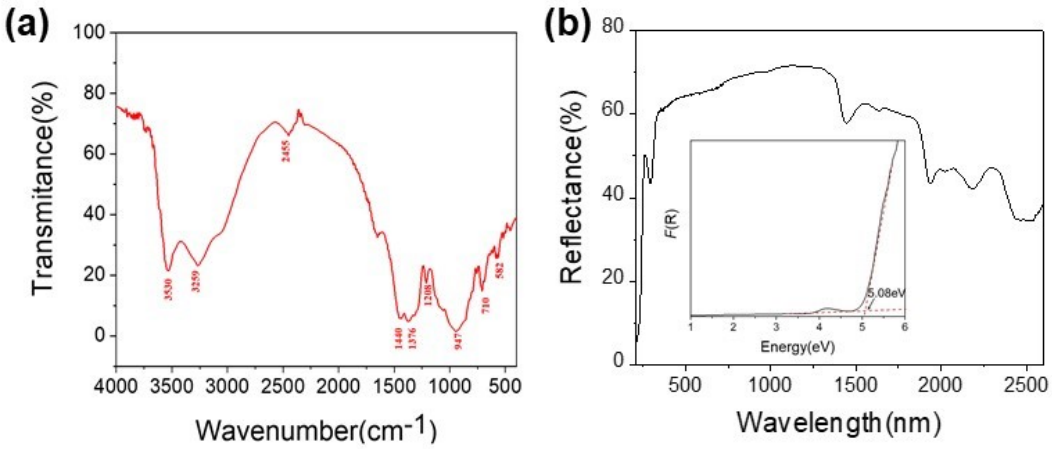

Figure S3. (a) infrared spectra and (b) UV-Vis-NIR diffuse reflectance of $Ba_2B_5O_8(OH)_2(NO_3)\cdot 3H_2O$

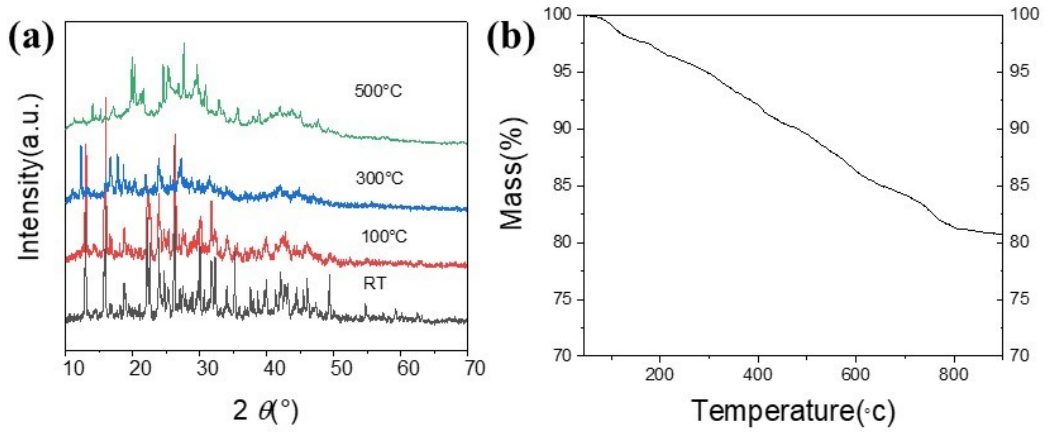

Figure S4. (a) PXRD and (b) TG curves of $Ba_2B_5O_8(OH)_2(NO_3)\cdot 3H_2O$ at different temperatures.

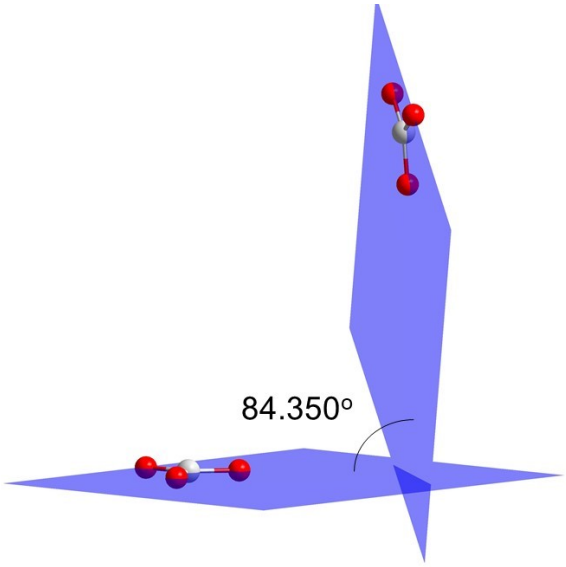

Figure S5. The dihedral angles of the nonparallel arrangement $[NO_3]^-$ anions