Supporting Information

Two novel metal borates with three-dimensional open-framework

layers constucted from the $[M_2B_8O_{20}(OH)_2]$ (M = Al, Ga) cluster units

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Figure S7. The IR spectra a) and TG curves b) of compounds 1 and 2.

Figure S8. The coordination environment of Ba atoms in 1, showing the Ba-O bond lengths from 2.704(6) to 3.088(4) Å. Two BaO₁₀ polyhedra link by two O4 atoms to form the Ba₂O₁₈ dimer. These dimers distribute in the 9-MR windows within the bilayer along the *c*-axis and link the adjacent bilayers.

Figure S9. View of the linking arrangement of Ba_2O_{18} dimers along the [110] direction, showing the hydrogen bonding interactions between Ba_2O_{18} dimers.

1. Synthesis of Ba[AlB₄O₈(OH)]·H₂O (1) and Ba[GaB₄O₈(OH)]·H₂O (2).

All reagents were analytically pure from commercial sources and used as received. The title compounds were synthesized by mild hydro(solvo)thermal method. A mixture of Al(i-PrO)₃ (aluminium isopropoxide) (1.0 mmol, 0.209 g) for **1** and Ga(i-PrO)₃ (gallium isopropoxide) (1.0 mmol, 0.242 g) for **2**, H₃BO₃ (10.0 mmol, 0.613 g), Ba(OH)₂·8H₂O (1.5 mmol, 0.480 g) was dispersed in a mixture of H₂O (4.0 mL) and pyridine (1.0 mL) and was stirred for about one hour. Then the mixture was sealed in an autoclave equipped with a Teflon liner (25 mL) heated at 260°C for 6 days under autogenous pressure. After cooling to room temperature, colorless irregular hexagonal flaky crystals of **1** and polygonal flaky crystals of **2** were obtained by sonication, then washed with distilled water and dried in air (the yields were about 82% based on Al for **1** and 85% based on Ga for **2**). The inductively coupled plasma emission spectroscopy indicate that the ratios of B:Al:Ba and B:Ga:Ba in **1** and **2** are 3.89:1.0:1.0 and 3.97:1.0:1.0, respectively.

2. Instrumentations for physical property measurements.

X-ray diffraction data collections were performed on a Rigaku SCXMini CCD diffractometer, equipped with a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at room temperature 293(2) K. Multi-scan method was used for the absorption correction.^[1] The structure was solved by the direct method and refined on F² by full-matrix least-squares methods using the SHELX-97 program package.^[2, 3] Powder X-Ray diffraction patterns were obtained using a Philips X'Pert-MPD diffractometer with CuK_{α} radiation ($\lambda = 1.54056$ Å) with a step size of 0.02°. IR spectra were obtained on an ABB Bomen MB 102 series FTIR spectrophotomete as KBr pellets in the range of 4000-500 cm⁻¹. The thermogravimetric analysis (TGA) was performed in a dynamic oxygen atmosphere with a heating rate of 10°C/min using a METTLER TGA/SDTA 851° thermal analyzer. The UV-Vis absorption and optical diffuse reflectance spectra were measured at room temperature using a Perkin-Elmer Lambda 900 UV-Visible spectrophotometer equipped with an integrating sphere attachment. BaSO₄ plate was used as a standard (100% reflectance).

^[1] CrystalClear, version 1.3.5; Rigaku Corp.: The Woodlands, TX, 1999.

^[2] Sheldrick, G. M. SHELXS-97, Program for Solution of Crystal Structures; University of Göttingen: Germany, 1997.

^[3] Sheldrick, G. M. SHELXS-97, Program for Solution of Crystal Refinement; University of Göttingen: Germany, 1997.

3. Tables and Figures

Compound	Ba[AlB ₄ O ₈ (OH)]·H ₂ O	Ba[GaB ₄ O ₈ (OH)]·H ₂ O
F_w	370.58	413.32
Crystal system	Monoclinic	Monoclinic
Space group	<i>C</i> 2/ <i>c</i> (No. 15)	<i>C</i> 2/ <i>c</i> (No. 15)
T/K	293(2)	293(2)
λ/Å	0.71073	0.71073
a/Å	12.509(8)	12.512(8)
<i>b</i> /Å	7.132(4)	7.125(4)
c/Å	19.316(11)	19.389(9)
β/deg	107.78(3)	107.30(4)
$V/Å^3$	1640.9(16)	1657.1(9)
Ζ	8	8
$D_{calcd}/g \cdot cm^{-3}$	3.000	3.313
μ (Mo-K α)/mm ⁻¹	4.989	8.016
Crystal size/mm ³	0.20 ×0.20 ×0.10	0.25 ×0.23 ×0.10
F (000)	1376	1520
GOF on F^2	1.092	1.070
$R_1, wR_2 (I > 2\sigma(I))^a$	0.0305, 0.0793	0.0233, 0.0542
R_1 , wR_2 (all data)	0.0339, 0.0996	0.0276, 0.0567

Table S1. Crystal data and structural refinements for $Ba[MB_4O_8(OH)] \cdot H_2O$ (M = Al, Ga).

 $\overline{{}^{a}R_{1} = \sum ||Fo| - |Fc|| / \sum |Fo|, wR_{2}} = \{\sum w[(Fo)^{2} - (Fc)^{2}]^{2} / \sum w[(Fo)^{2}]^{2} \}^{1/2}$

Table S2.	Selected bond	distances (Å	() for Ba	MB ₄ O ₈ (O	H)]·H ₂ O	(M = Al.)	Ga).

Compound 1		Compound 2		
Ba(1)-O(9)#1	2.781(4)	Ba(1)-O(9)#1	2.776(3)	
Ba(1)-O(1)#2	2.822(4)	Ba(1)-O(1)#2	2.857(3)	
Ba(1)-O(5)	2.837(4)	Ba(1)-O(5)	2.866(3)	
Ba(1)-O(2)#2	2.845(4)	Ba(1)-O(2)#2	2.798(3)	
Ba(1)-O(4)#3	2.900(4)	Ba(1)-O(4)#3	2.893(3)	
Ba(1)-O(3)#4	2.959(4)	Ba(1)-O(3)#4	2.961(3)	
Ba(1)-O(7)	3.020(4)	Ba(1)-O(7)	2.920(3)	
Ba(1)-O(4)#4	3.021(4)	Ba(1)-O(4)#4	2.954(3)	

Ba(1)-O(6)	3.088(4)	Ba(1)-O(6)	3.096(3)
Ba(1)-O(1W)	2.704(6)	Ba(1)-O(1W)	2.707(5)
Mean Ba-O	2.898(4)	Mean Ba-O	2.883(3)
Al(1)-O(2)#4	1.812(4)	Ga(1)-O(2)#4	1.873(3)
Al(1)-O(4)#5	1.815(4)	Ga(1)-O(4)#5	1.891(3)
Al(1)-O(7)	1.839(4)	Ga(1)-O(7)	1.904(3)
Al(1)-O(8)	1.889(4)	Ga(1)-O(8)	1.940(3)
Al(1)-O(7)#6	1.977(4)	Ga(1)-O(7)#6	2.057(3)
Mean Al-O	1.866(4)	Mean Ga-O	1.933(3)
B(1)-O(1)	1.479(6)	B(1)-O(1)	1.486(6)
B(1)-O(5)	1.495(6)	B(1)-O(5)	1.492(6)
B(1)-O(6)	1.484(6)	B(1)-O(6)	1.476(6)
B(1)-O(7)	1.474(6)	B(1)-O(7)	1.469(6)
Mean B-O (□)	1.483(6)	Mean B-O (□)	1.481(6)
B(2)-O(3)	1.407(6)	B(2)-O(3)	1.416(6)
B(2)-O(4)	1.361(6)	B(2)-O(4)	1.375(6)
B(2)-O(5)	1.368(6)	B(2)-O(5)	1.359(6)
B(3)-O(1)	1.381(6)	B(3)-O(1)	1.372(6)
B(3)-O(2)	1.343(6)	B(3)-O(2)	1.356(6)
B(3)-O(3)	1.415(6)	B(3)-O(3)	1.406(6)
B(4)-O(6)	1.400(6)	B(4)-O(6)	1.387(6)
B(4)-O(8)	1.350(7)	B(4)-O(8)	1.353(6)
B(4)-O(9)	1.391(7)	B(4)-O(9)	1.376(6)
Mean B-O (1.379(7)	Mean B-O (∆)	1.378(6)

Symmetry transformations used to generate equivalent atoms: #1 -*x*+1/2,*y*+1/2,-*z*+5/2; #2 *x*,*y*+1,*z*; #3 -*x*,-*y*+2,-*z*+2; #4 x+1/2,y+1/2,z; #5 x+1/2,y-1/2,z; #6 -*x*+1/2,-*y*+3/2,-*z*+2

Compound	Interaction	H•••A (Å)	D…A (Å)	Angle (°)	Symmetry codes
1	O9-H9AO8	1.94	2.750(5)	171.1	- <i>x</i> +1, <i>y</i> , - <i>z</i> +5/2
1	O1W-H1WAO8	2.38	3.252(9)	150.5	<i>x</i> , <i>y</i> +1, <i>z</i>
	O1W-H1WBO6	1.89	2.721(5)	142.7	- <i>x</i> +1/2, <i>y</i> +1/2, - <i>z</i> +5/2
2	O9-H9AO8	1.95	2.752(6)	167.7	- <i>x</i> +1, <i>y</i> , - <i>z</i> +5/2
2	O1W-H1WAO8	2.53	3.290(12)	149.8	<i>x</i> , <i>y</i> +1, <i>z</i>
	O1W-H1WBO6	1.98	2.709(7)	143.1	- <i>x</i> +1/2, <i>y</i> +1/2, - <i>z</i> +5/2

Table S3. Details of hydrogen bonds (Å) for $Ba[MB_4O_8(OH)] \cdot H_2O$ (M = Al, Ga).



Figure S1. a) Schematic drawing of a known $B_5O_9(OH)$ cluster; b) The $MB_4O_{11}(OH)$ (M = Al, Ga) cluster transferred by the $B_5O_9(OH)$ cluster through replacing a BO₃ by a O_2MO_3 group. Color code: O_2MO_3 fuchsia, BO₄ green, BO₃ yellow, similarly hereinafter.



Figure S2. a/b) The ball-and-stick representations of $MB_4O_{11}(OH)$ (M = Al, Ga) and $B_5O_9(OH)$ clusters.



Figure S3. a) Views of a single sheet (α + or α -) of MBO (M = Al, Ga), showing the 3- and 9-MRs windows. b) View of 3D bilayer along the *c*-axis. c) Schematic description of the common *sql* topological net for the single sheet. d) The *sql* topological net with the double edges for the bilayer (purple, M₂B₈ clusters; black/orange rods, O2/O4 linkers.



Figure S4. The simulated and experimental powder X-ray diffraction patterns of 1 and 2.

As shown in Figure 4a, the PXRD patterns tested at room temperature show the products 1 and 2 are in accordance with the calculated patterns based on the results from single-crystal X-ray diffraction, indicating the phase purity of the sample. To better understand the thermal behavior, the products 1 obtained after thermal annealing under different temperatures at a muffle furnace (5 hour for each step) were characterized by PXRD (Figure 4b), respectively. The series of diffraction peaks reveal that the fundamental packing is retained up to about 450°C. At the higher temperature (480°C), the compound was transformed into an amorphous phase completely.



Figure S5. The UV-vis absorption and Optical diffuse reflectance spectra of 1 a) and 2 b), respectively.

The UV-vis diffuse reflectance spectra of **1** and **2** show that the absorptions increase with the decreasing of wavelength. Absorption (K/S) data is calculated from the following Kubelka–Munk function: $\alpha/S = (1-R)^2/2R$,¹ where R is the reflectance, K is the absorption, and S is the scattering. The optical diffuse reflectance studies reveal that the band gaps for **1** and **2** are 5.57 and 5.33 eV, respectively. Comparing with values of other MBOs [Al(B₄O₉)(BO)]·H₂dap (dap=1,3-diaminopropane, 4.23 eV), K₂Al[B₅O₁₀]·4H₂O (4.45 eV),² Rb₂Ga(B₅O₁₀)(H₂O)₄ (3.76 eV),³ and borates β -BaB₂O₄ (BBO, 6.43 eV) and LiB₃O₅ (LBO, 7.78 eV),⁴ they also exhibit the property of wide-band-gap semiconductors.

^[1] W. W. Wendlandt, H. G. Hecht, Reflectance Spectroscopy, Interscience Publishers, New York, 1966.

^[2] C. Rong, Z.-W. Yu, Q. Wang, S.-T. Zheng, C.-Y. Pan, F. Deng, G.-Y. Yang, Inorg. Chem., 2009, 48, 3650.

^[3] T. Hu, C.-L. Hu, F. Kong, J.-G. Mao, T. C. W. Mak, Inorg. Chem., 2012, 51, 8810.

 ^{[4] (}a) C.-T. Chen, B.-C. Wu, A.-D. Jiang, G.-M. You, Sci. Sin., Ser. B, 1985, 28, 235. (b) C.-T. Chen, Y.-C. Wu, A.-D. Jiang, B.-C. Wu, G.-M. You, R.-K. Li, S.-J. Lin, J. Opt. Soc. Am. B, 1989, 6, 616. (c) R. H. French, J.-W. Ling, F. S. Ohuchi, C.-T. Chen, Phys. Rev. B., 1991, 44, 8496.



Figure S6. a/c) Calculated band structures of 1/2. b/d) The total density of states (DOS) and partial density of states (PDOS) of 1/2. The Fermi level was set to zero energy and marked as black curves. Red, blue and green curves represent the s-, p-, and -d orbits of PDOS of B, O, Al, Ga and Ba atoms, respectively.

Computational description

The band structures and density of states (DOS) of the compounds **1** and **2** were theoretically calculated by utilization the CASTEP code of MS. The total energy calculated within the density functional theory (DFT) using Perdew and Wang within generalized gradient approximation (GGA). The following orbital electrons are treated as valences: B $2s^22p^1$, O $2s^22p^4$, Al $3s^23p^1$, Ga $4s^24p^1$, Ba $5s^25p^66s^2$. The number of plane waves included in the basis is determined by the cutoff energy of 450.0 eV, and the numerical integration of the Brillouin zone is performed a Monkhorst-Pack *k* point sampling of $5 \times 5 \times 5$. The other calculation parameters and convergent criteria were the default values of CASTEP code.



Figure S7. The IR spectra a) and TG curves b) of compounds 1 and 2.

As shown in Figure S7a, the adsorption peaks around 1457-1226 cm⁻¹ mainly attribute to the BO₃ antisymmetric stretching vibrations (B-O), while those near 1178-1038 cm⁻¹ should be assigned to BO₄ antisymmetric stretch vibrations (B-O). The bands associated with BO₃ and BO₄ out of plane bending modes are overlapped and located about 863–820 cm⁻¹. The Al-O and Ga-O vibrations are assigned to 931, 863, 542 cm⁻¹ and 920, 856, 518 cm⁻¹, respectively. In addition, the characteristics of the O–H groups are observed at 3420 and 1616 cm⁻¹. Figure S7b shows that the weight losses are assigned to the removal of water molecules and the dehydration of the –OH groups.



Figure S8. The coordination environment of Ba atoms in 1, showing the Ba-O bond lengths from 2.704(6) to 3.088(4) Å. Two BaO₁₀ polyhedra link by two O4 atoms to form the Ba₂O₁₈ dimer. These dimers distribute in the 9-MR windows within the bilayer along the *c*-axis and link the adjacent bilayers.



Figure S9. View of the linking arrangement of Ba_2O_{18} dimers along the [110] direction, showing the hydrogen bonding interactions between Ba_2O_{18} dimers.