

Electronic Supporting Information

Two Layered Galloborates from Centric to Acentric Structures: Syntheses and NLO Property

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Experimental Section

Syntheses: In the typical syntheses of **1**, the powder mixture of H₃BO₃ (0.248 g, 4 mmol), Na₂CO₃ (0.046 g, 0.44 mmol), Ba(OH)₂·8H₂O (0.315 g, 1 mmol) and Ga(i-Pro)₃ (0.123 g, 0.5 mmol) were added in the mixed solution of 2 mL pyridine and 1 mL H₂O, and stirred for one hour. The final mixed solution was sealed in a 23-mL Teflon-lined stainless-steel reactor and heated at 210 °C for 7 days. After cooling down to room temperature, block-like colorless crystals of **1** were obtained. (Yield: 45.0% basing on Na₂CO₃). By raising the B/Ga ratio in the reactants from 8:1 to 16:1 (8 mmol H₃BO₃ and 0.5 mmol Ga(i-Pro)₃) and raising the temperature from 210 to 230 °C with other conditions unchanged, flake-like colorless crystals of **2** was obtained. (Yield: 27.0% basing on Na₂CO₃). Ba(OH)₂ is used as mineralizer. Strong alkalis are commonly used mineralizers in hydro(solvo)thermal syntheses of borates, especially in the mid/low-temperature hydro(solvo)thermal conditions.¹⁻³ Using the same B/Ga ratio of 16:1 and the temperature of 210 °C, **2** cannot be obtained.

[1] C. McMillen, C. Heyward, H. Giesber and J. Kolis, *J. Solid. State. Chem.*, 2011, **184**, 2966-2971.

[2] X. F. Wang, F. F. Zhang, B. H. Lei, Z. H. Yang and S. L. Pan, *RSC Adv.*, 2016, **6**, 100849-100856.

[3] C. C. Peng, H. K. Liu and K. H. Lii, *Inorg. Chem.*, 2018, **57**, 1545-1549.

Single-crystal X-ray diffraction data of **1** and **2** were collected on a Gemini A Ultra and Bruker APEX-II diffractometer using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293K, respectively. The structure was solved by direct methods and refined by full-matrix least-squares fitting on F² methods with SHELXTL-2013 program.¹ PLATON was used for checking higher structural symmetries and no higher symmetries were found.² Absorption corrections were conducted by multi-scan methods for **1** and **2**. Anisotropic displacement parameters were refined for all atoms except for hydrogen atoms. Hydrogen atoms were geometrically placed and refined by riding model. Detailed crystallographic data and structure refinement were summarized in Table S1. CCDC 2145342 (**1**) and 2145343 (**2**) contain the detailed crystallographic data for this paper.

All the reagents were analytical grade and used without any further purification. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) in the angular range of $2\theta = 5\text{--}50^\circ$. Thermogravimetric analyses were conducted on a Mettler Toledo TGA/DSC 1100 analyzer in the air atmosphere heating up from 25 to 1000 °C, raising 10 °C per min. UV-Vis spectra were recorded on a Shimadzu UV3600 spectrometer with the wavelengths scanning from 190 to 800 nm. Infrared spectra were recorded on a Nicolet iS10 FT-IR spectrometer with the wavenumbers ranging from 4000-400 cm⁻¹.

SHG measurements were conducted on a Q-switched Nd:YAG laser with the fundamental light wavelength of 1064 nm. The single crystal samples of **2** and KDP (standard sample) were sieved into five different sizes: 25–45, 45–62, 62–75, 75–109 and 109–150 μm . The samples were pressed between two rounded 1 mm thick quartz glasses

with a 2 mm thick rubber ring interlayer. The diameter of the spot area is about 8mm. The samples are tightly sealed in an aluminous round box with an 8mm diameter hole in the center. The laser power density is 35 MW/cm². The intensities of the harmonic generation signals were measured by a photomultiplier tube attached to a RIGOL DS1052E 50 MHz oscilloscope.

[1] a) G. M. Sheldrick, *SHELXTL-97, Program for Solution of Crystal Structures; University of Göttingen: Germany 1997*; b) G. M. Sheldrick, *SHELXS-97, Program for Solution of Crystal Refinement; University of Göttingen: Germany 1997*.

[2] A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.

Table S1 Crystallographic data and structural refinements for **1-2**.

	1	2
Empirical formula	Na ₃ GaB ₄ O ₉	Na ₅ GaB ₁₆ O ₃₂ H ₈
Formula weight	325.93	877.69
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>C</i> ₂
<i>a</i> /Å	6.2135(12)	16.5740(5)
<i>b</i> /Å	8.6750(18)	7.3430(2)
<i>c</i> /Å	6.7916(12)	11.7190(4)
α /°	90	90
β /°	99.265 (16)	114.622(6)
γ /°	90	90
<i>V</i> /Å ³	361.31 (12)	1296.4(7)
<i>Z</i>	2	2
<i>D_c</i> /g cm ⁻³	2.996	2.248
μ /mm ⁻¹	4.023	1.285
<i>F</i> (000)	312	860
Diffractive Indices	-8≤ <i>h</i> ≤6, -10≤ <i>k</i> ≤11, -8≤ <i>l</i> ≤9	-18≤ <i>h</i> ≤19, -8≤ <i>k</i> ≤8, -14≤ <i>l</i> ≤13
Goodness-of-fit on <i>F</i> ²	1.088	1.029
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	0.0279 (0.0700)	0.0482 (0.0958)
<i>R</i> indices (all data)	0.0297 (0.0715)	0.0725 (0.1033)
Largest Peak/Deepest hole	0.632/-0.900	0.455/-0.585
[e·Å ⁻³]		

^a*R*₁ = $\sum ||F_o| - |F_c| | / \sum |F_o|$. *wR*₂ = $\{\sum w[(F_o)^2 - (F_c)^2]^2 / \sum w[(F_o)^2]^2\}^{1/2}$

Table S2. Hydrogen bond distances (Å) and angles (°) for the compound **2**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA) (°)
O(7)–H(1)···O(1)#1	0.86	1.94	2.7593	158.7
O(7)–H(1)···O(16)#2	0.86	2.55	3.1314	126.0
O(11)–H(11)···O(16)#2	0.82	2.06	2.8194	153.0
O(12)–H(12)···O(1)#2	0.86	2.55	3.3377	154.0
O(13)–H(13)···O(15)#2	0.85	2.11	2.8081	139.0

Symmetric codes: #1: 1/2-x, -1/2+y, -z; #2: 1/2+x, 1/2+y, z.

Table S3. Selected bond lengths (Å) and angles (°) for compound **1**.

Bond Lengths (Å)		Bond Angles (°)	
Ga1-O1	1.824	O1-Ga1-O4 ²	112.05
Ga1-O4 ²	1.853	O1-Ga1-O4 ³	109.84
Ga1-O4 ³	1.853	O1-Ga1-O6 ⁴	109.87
Ga1-O6 ⁴	1.821	O4 ² -Ga1-O6 ⁴	111.38
B1-O1	1.445	O4 ³ -Ga1-O6 ⁴	111.38
B1-O2	1.501	O4 ² -Ga1-O4 ³	99.82
B1-O2 ¹	1.501	O1-B1-O3	109.77
B1-O3	1.439	O1-B1-O2	110.40
B2-O2	1.381	O1-B1-O2 ¹	110.40
B2-O4	1.368	O2-B1-O3	108.31
B2-O5	1.368	O2 ¹ -B1-O3	108.31
B3-O3	1.420	O2-B1-O2 ¹	109.57
B3-O5	1.526	O2-B2-O4	118.62
B3-O5 ¹	1.526	O2-B2-O5	121.47
B3-O6	1.427	O4-B2-O5	119.86
Na1-O1	2.556	O3-B3-O5	110.38
Na1-O3	2.177	O3-B3-O5 ¹	110.38
Na1-O4 ⁵	2.498	O3-B3-O6	114.09
Na1-O4 ⁶	2.498	O5-B3-O6	108.42
Na1-O5 ⁷	2.333	O5 ¹ -B3-O6	108.42
Na1-O5 ⁸	2.333	O5-B3-O5A	104.68
Na2-O1 ⁹	2.492		
Na2-O2 ⁶	2.600		
Na2-O2 ¹⁰	2.363		
Na2-O4 ¹¹	2.404		
Na2-O5	2.551		
Na2-O6	2.293		

Symmetry codes: **1:** x, 0.5-y, z; **2:** 1-x, 1-y, 2-z; **3:** 1-x, -0.5+y, 2-z; **4:** x, y, 1+z; **5:** 1-x, -0.5+y, 1-z; **6:** 1-x, 1-y, 1-z; **7:** -1+x, 0.5-y, z; **8:** -1+x, y, z; **9:** 1-x, 0.5+y, 1-z; **10:** x, y, -1+z; **11:** 2-x, 1-y, 1-z.

Table S4. Selected bond lengths (Å) and angles (°) for compound **2**.

Bond Lengths		Bond Lengths		Bond Angles	
Ga1-O1 ¹	1.817	Na1-O7 ⁵	2.320	O3-B3-O15	113.47
Ga1-O1 ²	1.817	Na1-O9	2.253	O4-B3-O5	108.67
Ga1-O16	1.853	Na1-O16 ⁶	2.379	O5-B3-O15	107.58
Ga1-O16 ³	1.821	Na2-O1 ⁷	2.548	O4-B3-O15	111.00
B1-O1	1.386	Na2-O2	2.397	O6-B4-O7	120.34
B1-O2	1.360	Na2-O6	2.513	O6-B4-O8	125.03
B1-O3	1.352	Na2-O6 ⁸	2.543	O7-B4-O8	114.62
B2-O2	1.430	Na2-O11	2.370	O5-B5-O8	106.10
B2-O5	1.505	Na2-O12 ⁷	2.515	O5-B5-O9	105.39
B2-O6	1.461	Na2-O14 ⁸	2.466	O5-B5-O10 ⁴	110.33
B2-O14	1.476	Na3-O8	2.527	O8-B5-O9	110.75
B3-O3	1.458	Na3-O8 ⁹	2.527	O8-B5-O10 ⁴	110.80
B3-O4	1.468	Na3-O13 ¹⁰	2.364	O9-B5-O10 ⁴	113.12
B3-O5	1.526	Na3-O13 ¹	2.364	O4-B6-O9	122.99
B3-O15	1.448			O4-B6-O10	119.17
B4-O6	1.350			O9-B6-O10	117.79
B4-O7	1.383			O14-B7-O15	124.87
B4-O8	1.382			O14-B7-O16	118.12
B5-O5	1.527			O15-B7-O16	117.00
B5-O8	1.470			O11-B8-O12	115.60
B5-O9	1.447			O11-B8-O13	124.85
B5-O10 ⁴	1.429			O12-B8-O13	119.53
B6-O9	1.371				
B6-O10	1.374				
B6-O4	1.375				
B7-O14	1.356				
B7-O15	1.362				
B7-O16	1.384				
B8-O11	1.361				
B8-O12	1.387				
B8-O13	1.375				
Na1-O3 ⁴	2.343				
Na1-O4 ⁴	2.494				

Bond Angles	
O1 ¹ -Ga1-O1 ²	113.50
O1 ¹ -Ga1-O16	113.75
O1 ¹ -Ga1-O16 ³	101.21
O1 ² -Ga1-O16	101.21
O1 ² -Ga1-O16 ³	113.75
O16-Ga1-O16 ³	114.01
O1-B1-O2	117.90
O1-B1-O3	117.83
O2-B1-O3	124.26
O2-B2-O5	109.15
O2-B2-O6	110.28
O2-B2-O14	112.32
O5-B2-O6	108.32
O6-B2-O14	109.11
O5-B2-O14	107.55
O3-B3-O4	109.04
O3-B3-O5	106.90

Symmetry codes: **1:** x, -1+y, z; **2:** -x, -1+y, -z; **3:** -x, y, -z; **4:** 0.5-x, -0.5+y, 1-z; **5:** 1-x, y, 1-z; **6:** 0.5-x, 0.5+y, 1-z; **7:** 0.5-x, -0.5+y, -z; **8:** 0.5-x, 0.5+y, -z; **9:** 1-x, y, 1-z; **10:** 1-x, -1+y, 1-z.

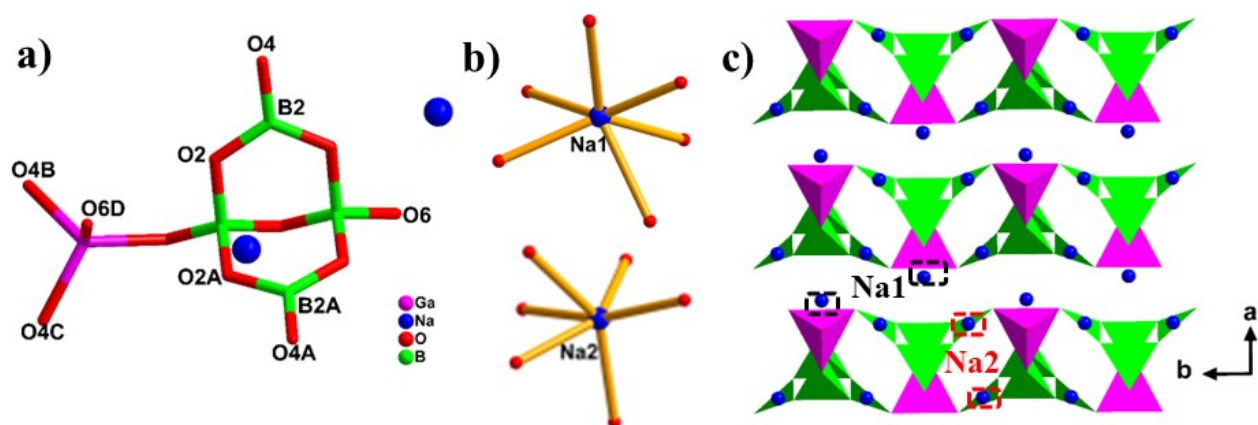


Figure S1. a) Asymmetric unit of **1**; b) $\text{Na}_1\text{O}_6/\text{Na}_2\text{O}_6$ polyhedra in **1**; c) Locations of $\text{Na}^{1+}/\text{Na}^{2+}$ in the framework of **1**.

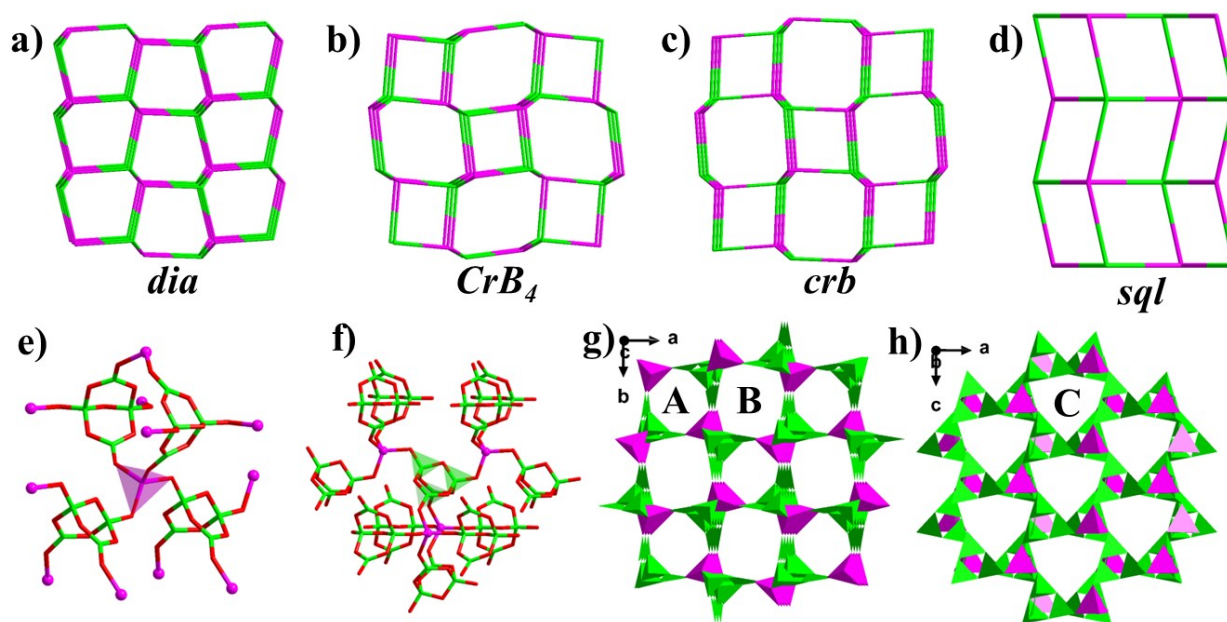


Figure S2. a) 3D *dia* framework of $\text{K}_2\text{GeB}_4\text{O}_9 \cdot 2\text{H}_2\text{O}$; b) 3D CrB_4 framework of $\text{GeB}_4\text{O}_9 \cdot \text{H}_2\text{en}$; c) 3D *crb* framework of **3**; d) 2D *sql* layer of **1**; e) Coordination environment of GaO_4 unit in **3**; f) Coordination environment of B_4O_9 unit in **3**; g-h) View of the 3D open frameworks of **3** along different axes.

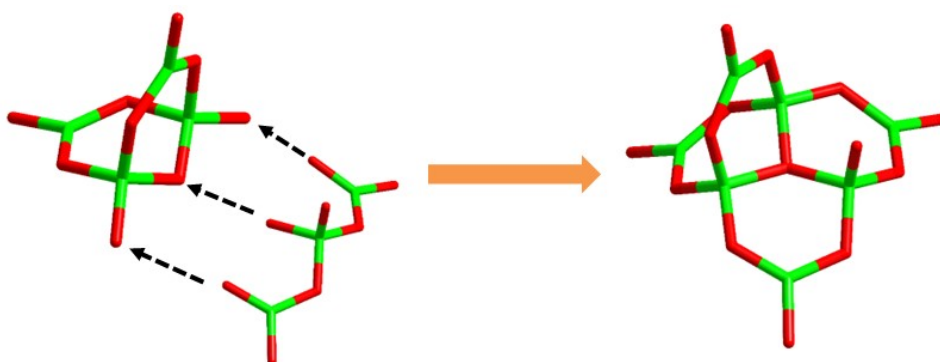


Figure S3. The further polymerization from B_4O_9 cluster to $\text{B}_7\text{O}_{13}(\text{OH})$ cluster. H atom is omitted for clarity.

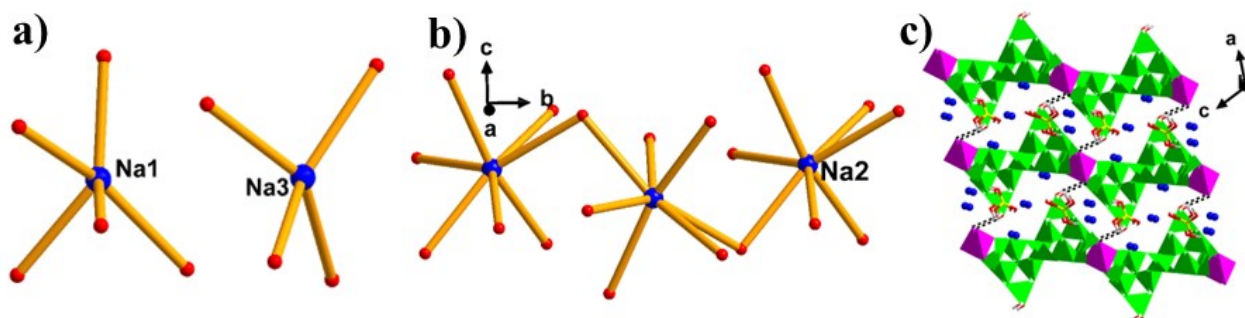


Figure S4. a) Na1O_5 and Na3O_4 polyhedra in **2**; b) Na2O_7 polyhedra the 1D Na2-O chain in **2**; c) 3D supramolecular framework of **2** with guest Na^+ and B(OH)_3 molecules locate in the layer and interlayer.

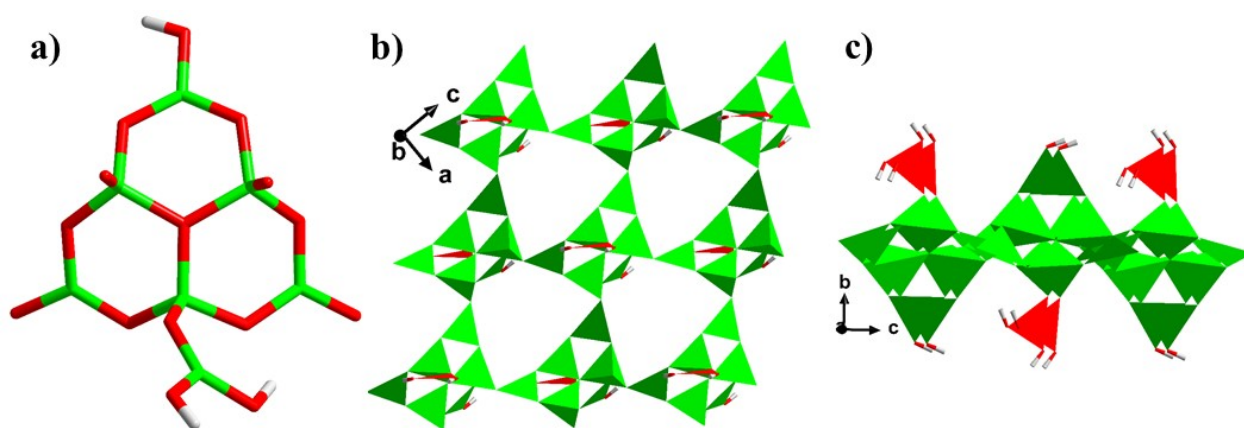


Figure S5. a) The $\text{B}_7\text{O}_{12}(\text{OH})_3$ cluster in $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3][\text{B}_7\text{O}_{10}(\text{OH})_3]$; b) 2D monolayer with 9-MR windows in $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3][\text{B}_7\text{O}_{10}(\text{OH})_3]$; c) Side view of the layer in $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3][\text{B}_7\text{O}_{10}(\text{OH})_3]$.

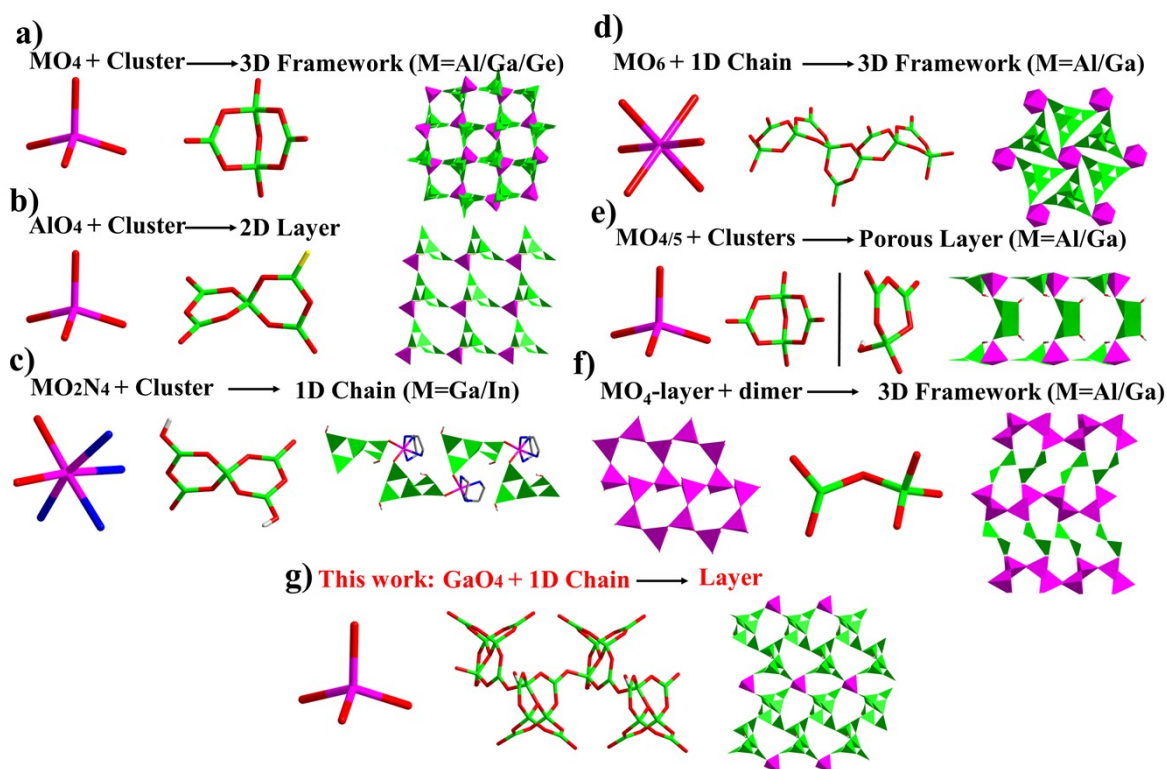


Figure S6. a-f) Six known different linkages between MO_n ($n=4/5/6$) polyhedra and oxoboron clusters; g) The new linkage of GaO_4 and 1D oxoboron cluster-chain in **2**.

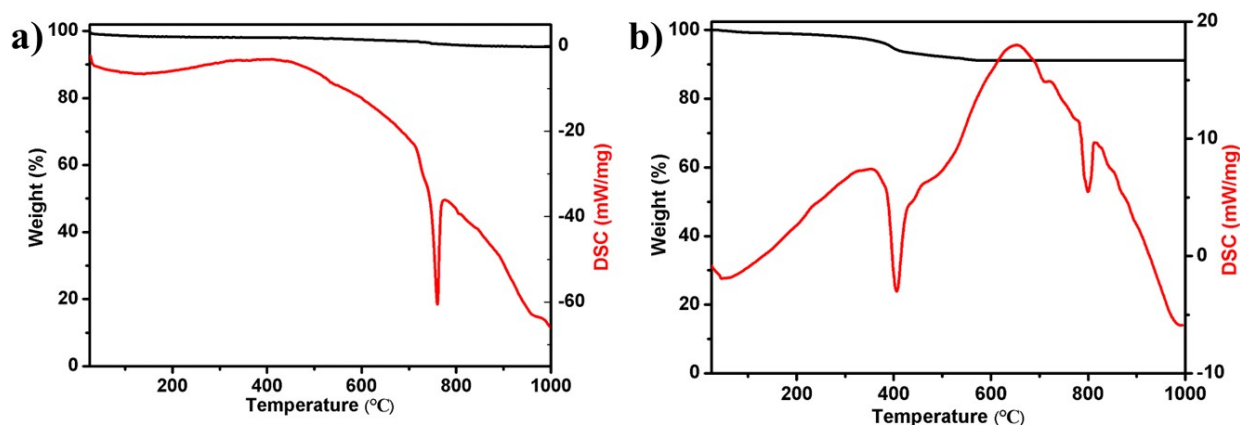


Figure S7. TG-DSC curves of **1**(a) and **2**(b).

For **1**, there is no obvious weight loss from 25-739°C. The minor weight loss of 3.17% from 739-777°C with the endothermic peak at 757°C indicate that the samples start to melt from 739°C, accompanied with the volatilization of partial B_2O_3 residues ($1.5Na_2O \cdot 0.5Ga_2O_3 \cdot 2B_2O_3$).

For **2**, the total weight loss of 8.78% (calculated: 8.20%) from 350-450°C of **2** is attributed to the 4 H_2O from the dehydrations of 2 -OH groups and 2 boric acid molecules, corresponding to the first endothermic peak at 407°C on the DSC curve. The second endothermic peak at 798°C on the DSC curve is attributed to the melting of the residues ($2.5Na_2O \cdot 0.5Ga_2O_3 \cdot 8B_2O_3$).

For further investigating the thermal stabilities of **1** and **2**, the residues after TGA/DSC measurements were checked by PXRD patterns and IR spectra. PXRD patterns show that the residues of both **1** and **2** are amorphous and IR spectra show that the frameworks of **1** and **2** have collapsed after thermal treatments.

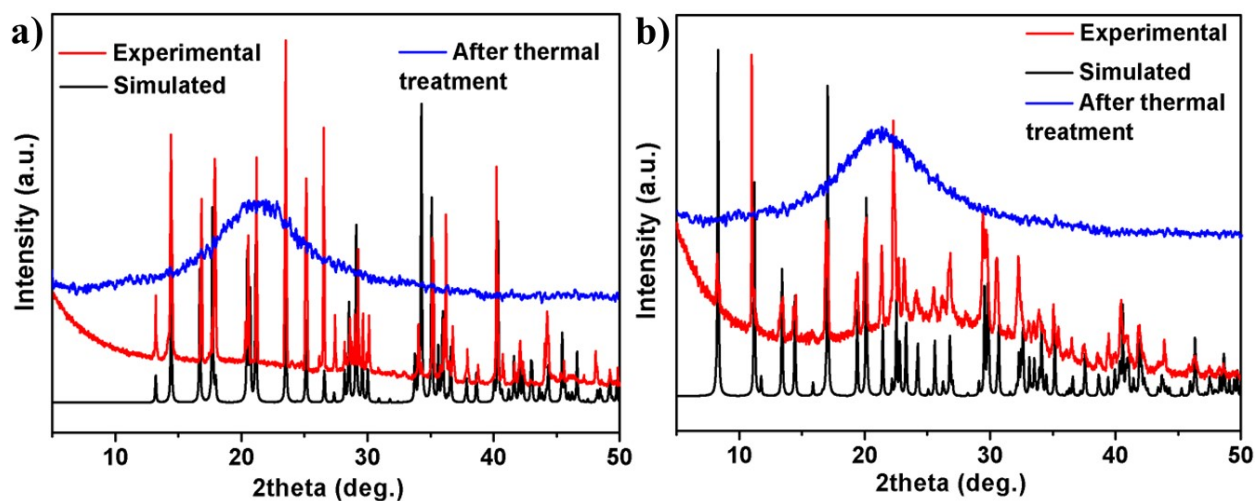


Figure S8. PXRD patterns before and after thermal treatments of **1** (a) and **2** (b).

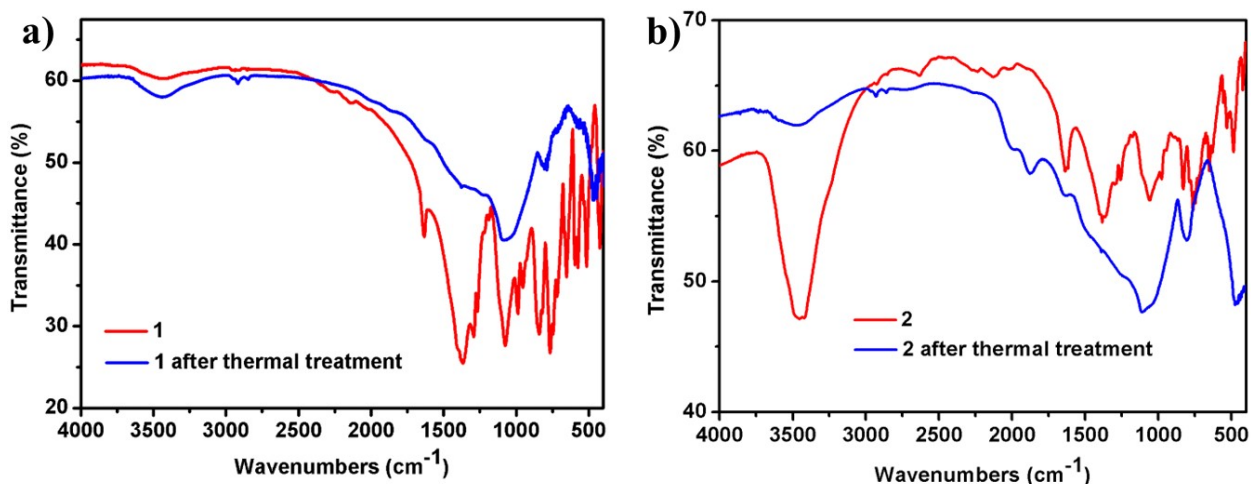


Figure S9. IR spectra of **1** (a) and **2** (b).

The IR spectra of **1** and **2** confirm the existences of BO_3 , BO_4 and $-\text{OH}$ groups. The absorption peaks from $1468\text{--}1248\text{ cm}^{-1}$ and $1127\text{--}915\text{ cm}^{-1}$ are the asymmetric stretching vibrations of BO_3 and BO_4 groups, respectively. The peak at 3452 cm^{-1} for **2** is assigned to the asymmetric stretching vibrations of $-\text{OH}$ groups. The inconsistencies of the peaks between samples before and after thermal treatments indicate that the frameworks of **1** and **2** have collapsed.

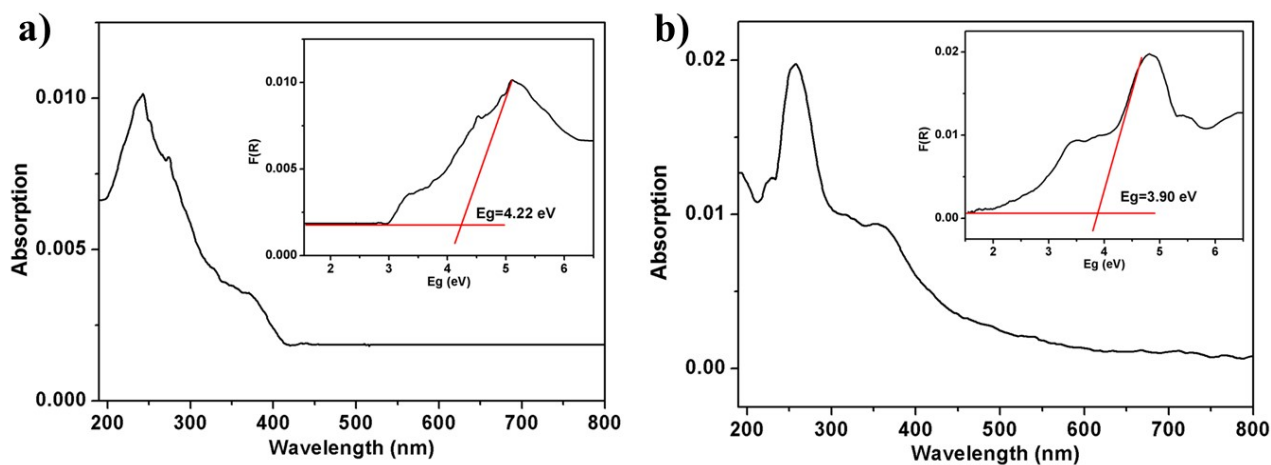


Figure S10. UV-Vis spectra of **1** (a) and **2** (b).

UV-Vis absorption spectra show that the band gaps of **1** and **2** are 4.22 and 3.90 eV, respectively, indicating that they are wide-band semiconductors. The small absorptions observed around 360nm can be attributed to the impurities of the raw materials or from their extrinsic midgap states, which appeared in other reported GBOs.^{1,2}

[1] J. Sun, M. Mutailipu and S. L. Pan, *Chem. Eur. J.*, 2021, **27**, 8698-8703.

[2] W. L. Gao, Y. Jing, J. Yang, Z. Y. Zhou, D. F. Yang, J. L. Sun, J. H. Lin, R. H. Cong and T. Yang, *Inorg. Chem.*, 2014, **53**, 2364–2366.