Supporting Information

Centrosymmetric $(Hdima)_2[Ge_5B_3O_{15}(OH)]$ and Noncentrosymmetric $Na_4Ga_3B_4O_{12}(OH)$: Solvo/Surfactant-Thermal Synthesis of Open-Framework Borogermanate and Galloborate

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Experimetal Section

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Synthesis of **1**. A mixture of GeO_2 (1 mmol, 0.1046 g) (99.999%), H_3BO_3 (10 mmol, 0.6183 g) (99.5%), DMA (5 ml) (99.0%) and dimethylamine (1 ml) (33.0%) was sealed in a 30 mL Teflon-lined bomb at 170 ℃ for 6 days and then cooled to room temperature. Colorless block crystals of **1** were obtained by filtration, washed with distilled water, and dried in air (25% yield based on GeO_2). Elemental analysis calcd (%) for $C_4H_{17}B_3Ge_5N_2O_{16}$: C 6.45, H 2.30, N 3.76; found: C 6.46, H 2.23, N 3.47. IR (KBr, cm^{-1}): 3242(m), 3039(m), 2790(m), 2510(w), 1635(w), 1600(w), 1469(w), 1405(w), 1356(w), 1030(m), 884(s), 828(s), 565(m), 523(w) (Figure. S3).

Synthesis of **2**. A mixture of $NaBO_2 \cdot 4H_2O$ (2 mmol, 0.308 g) (99.0%), Ga_2O_3 (0.5 mmol, 0.094 g) (99.99%), dimethylamine (1mL) (33.0%) and polyethylene glycol-200 (PEG-200, 5 mL) (99.5%) (pH = 9) was sealed in a 30 mL Teflon-lined bomb at 170 ℃ for 6 days and then cooled to room temperature. Colorless cubic crystals of **2** were obtained by filtration, washed with distilled water, and dried in air (18% yield based on Ga_2O_3). IR (KBr, cm^{-1}): 3440(s), 1628(m), 1285(vs), 715(vs) (Figure. S3).

Table S1. X-ray crystallographic data for **1** and **2**.

Empirical formula	$C_4H_{17}B_3Ge_5N_2O_{16}$	$B_4Ga_3HNa_4O_{13}$
M_r	744.58	553.37
crystal system	Triclinic	cubic
space group	*P*-1	*F-43c*
a (Å)	8.0917(2)	13.6737(2)
b (Å)	9.0697(3)	13.6737(2)
c (Å)	14.3025(4)	13.6737(2)
α (^{o})	97.213(2)	90
β (^{o})	101.552(2)	90
γ (^{o})	105.263(2)	90
V (Å^3)	974.31(5)	2556.57(6)
Z	2	8
D_c (g cm^{-3})	2.538	2.875
μ (mm^{-1})	7.705	6.482
F(000)	716	2096
crystal size (mm)	0.16×0.14×0.08	0.15× 0.15 × 0.15
index ranges	1.48-27.66	2.98-27.47
GOF	1.024	1.201
collected reflcns	33417	8516
unique reflcns (R_{int})	4544 (0.0653)	257 (0.0302)
observed reflcns [$I > 2\sigma(I)$]	3745	242
refined parameters	276	27
R_1[a]/wR_2[b] [$I > 2\sigma(I)$]	0.0296/0.0615	0.0233/0.0717
R_1[a]/wR_2[b] (all data)	0.0421/0.0658	0.0242/0.0730
largest difference peak/hole	0.585/-0.580	0.767/ -0.580

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b] $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S2. Selected bond lengths (Å) and bond valence sum (BVS) calculations for compound **1**[a].

Bond	Distance (Å)	BVS	BVS (Sum)	Bond	Distance (Å)	BVS	BVS (Sum)
Ge(1)-O(5)	1.730(3)	1.063	4.035	Ge(5)-O(15)	1.733(3)	1.053	4.105
Ge(1)-O(9)	1.741(3)	1.028		Ge(5)-O(16)	1.736(2)	1.043	
Ge(1)-O(16A)	1.754(3)	0.988		Ge(5)-O(14)	1.741(3)	1.027	
Ge(1)-O(6)	1.765(3)	0.956		Ge(5)-O(12)	1.756(3)	0.982	
Ge(2)-O(8)	1.714(3)	1.115	4.170	B(1)-O(1)	1.362(5)	1.011	2.991
Ge(2)-O(15B)	1.737(3)	1.040		B(1)-O(2)	1.366(5)	0.999	
Ge(2)-O(7)	1.744(3)	1.018		B(1)-O(3)	1.373(5)	0.981	
Ge(2)-O(6)	1.751(3)	0.997		B(2)-O(4)	1.456(5)	0.784	2.990
Ge(3)-O(10)	1.729(3)	1.066	4.044	B(2)-O(2)	1.468(5)	0.759	
Ge(3)-O(9)	1.734(3)	1.049		B(2)-O(5)	1.475(5)	0.745	
Ge(3)-O(14)	1.759(3)	0.973		B(2)-O(13A)	1.497(4)	0.702	
Ge(3)-O(11)	1.765(3)	0.956		B(3)-O(4)	1.455(5)	0.786	2.991
Ge(4)-O(13)	1.731(3)	1.060	4.079	B(3)-O(3)	1.471(5)	0.753	
Ge(4)-O(7C)	1.734(3)	1.049		B(3)-O(10A)	1.479(4)	0.737	
Ge(4)-O(12)	1.753(3)	0.991		B(3)-O(8)	1.490(4)	0.715	
Ge(4)-O(11)	1.757(3)	0.979					

[a]Symmetry codes: A: *x* + 1, *y*, *z*; B: -*x* - 3, -*y*, -*z* + 2; C: *x* - 1, *y* - 1, *z*.

Table S3. Hydrogen bond lengths (Å) and bond angles (^{o}) in compound **1**[a].

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠ (DHA)
O(1)-H(1)...O(3)#1	0.82	1.93	2.744(4)	169.1
N(1)-H(1D)...O(6)#1	0.90	2.24	3.056(4)	151.2
N(1)-H(1E)...O(10)#1	0.90	2.10	2.895(5)	147.6
N(2)-H(2E)...O(13)#1	0.90	1.87	2.766(4)	170.5
N(2)-H(2D)...O(2)#2	0.90	1.89	2.786(5)	172.2
N(1)-H(1E)...O(8)#3	0.90	2.12	2.898(5)	144.5

[a]Symmetry codes: #1: -*x* - 2, -*y* - 1, -*z* + 1; #2: *x* + 2, *y* + 1, *z*; #3: -*x* - 1, -*y*, -*z* +1.

Table S4. Selected bond lengths (Å) and bond valence sum (BVS) calculations for compound **2**[a].

Bond	Distance (Å)	BVS	BVS (Sum)	Bond	Distance (Å)	BVS	BVS (Sum)
Ga-O(1)	1.8345(18)	0.762	3.048	Na(1)-O(1D)	2.410(3)	0.182	1.196
Ga-O(1A)	1.8344(18)	0.762		Na(1)-O(1F)	2.410(3)	0.182	
Ga-O(1B)	1.8344(18)	0.762		Na(1)-O(2)	2.524(5)	0.141	
Ga-O(1C)	1.8344(18)	0.762		Na(1)-O(2E)	2.524(5)	0.141	
B-O(1)	1.3762(19)	0.971	2.913	Na(2)-O(2E)	2.490(14)	0.151	0.604
B-O(1)	1.3762(19)	0.971		Na(2)-O(2G)	2.490(14)	0.151	
B-O(1I)	1.3762(19)	0.971		Na(2)-O(2H)	2.490(13)	0.151	
Na(1)-O(1E)	2.2293(19)	0.275		Na(2)-O(2)	2.490(13)	0.151	
Na(1)-O(1)	2.2293(19)	0.275					

[a]Symmetry codes: A: -*y* + 1, *x* + 1, -*z* + 3/2; B: *y* - 1, -*x* + 1, -*z* + 3/2; C: -*x*, -*y* + 2, *z*; D: –*x* + 0, *z* + 0, -*y* + 3/2; E: *x*, -*y* + 3/2, -*z* + 3/2; F: –*x* + 0, -*z* + 3/2, *y* + 0; G: –*x* - 1/2, *y*, -*z* + 3/2; H: -*x* – 1/2, -*y* + 3/2, *z*; I: -*z* + 1/2, *x* + 1, -*y* + 3/2.

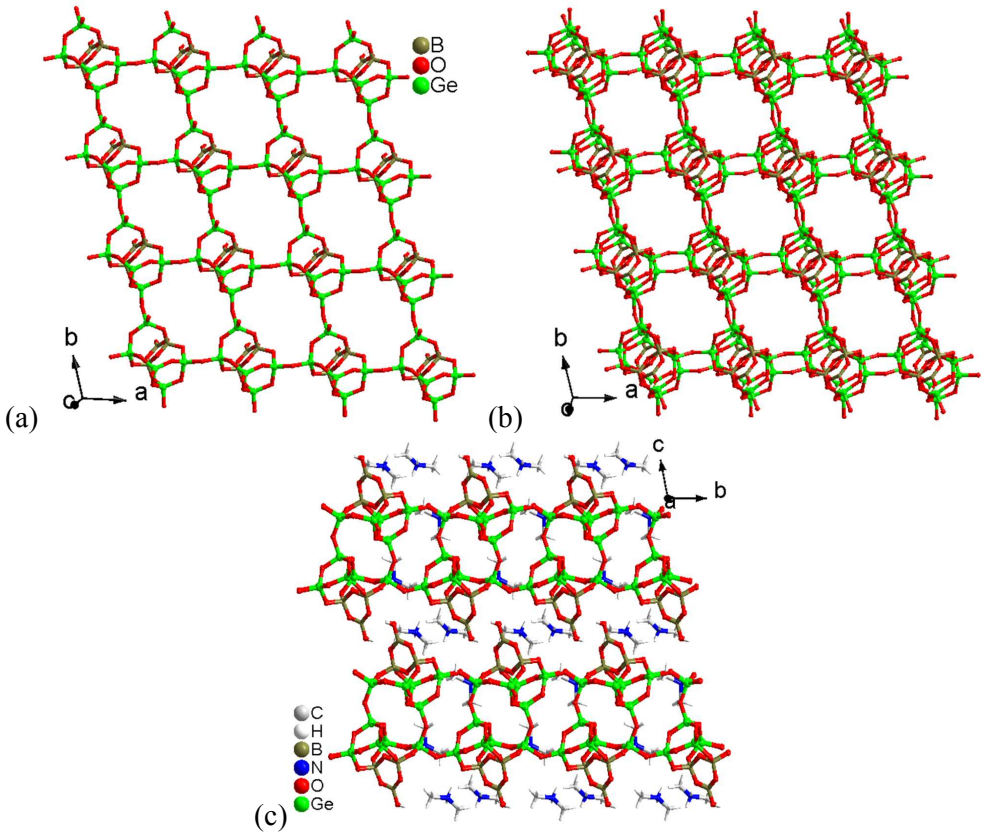

Figure S1. (a) View of the single sheet constructed by $Ge_5B_3O_{18}(OH)$ clusters in **1**; (b) View 10R channels along *c* axis in **1**; (c) The packing structure of **1** with 6R channels along the *a* axis. Organic templates are located in the porous layers and interlayers.

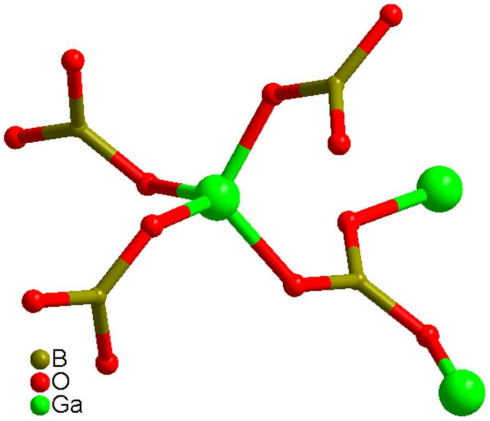

Figure S2. View of the linkage of BO_3 units and Ga^{3+} ions in **2**.

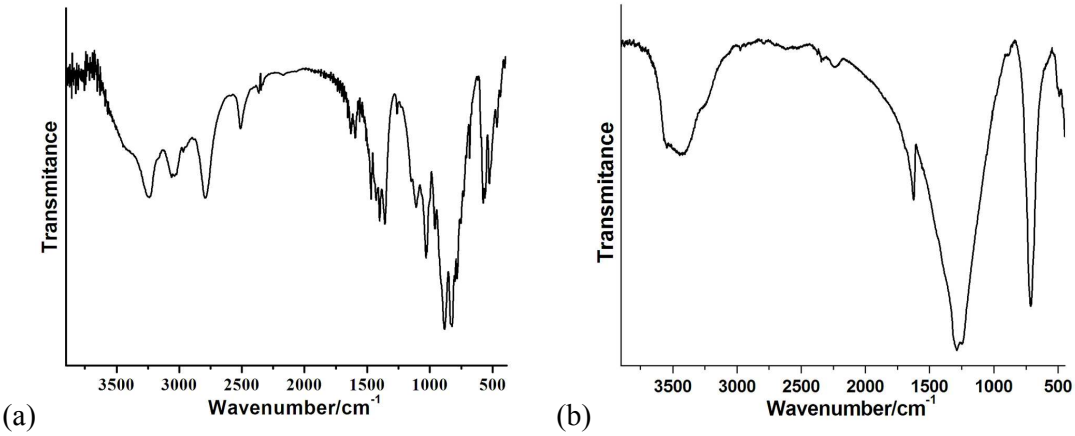

Figure S3. IR spectra of **1** (a) and **2** (b).

The IR spectrum of **1** show the presence of BO_3 triangles, BO_4 tetrahedra and GeO_4 tetrahedra in the structure. The IR spectrum of **1** displays strong absorption bands around 1356 cm^{-1} for the BO_3 groups. The bands for the BO_4 groups for both compounds appear around 1030 cm^{-1}. The absorption peaks around 828-884 cm^{-1} can be assigned to the asymmetrical stretch of the GeO_4 groups. The absorption bands of the symmetrical stretch of the Ge-O bonds are shown in the region of 523-565 cm^{-1}. The IR spectrum of **2** shows absorption band centered at 3440 and 1628 cm^{-1} can be assigned to the characteristic peak of OH vibration. Two sharp bands at 715 and 1285 cm^{-1} are attributed to the stretching and bending of BO_3.

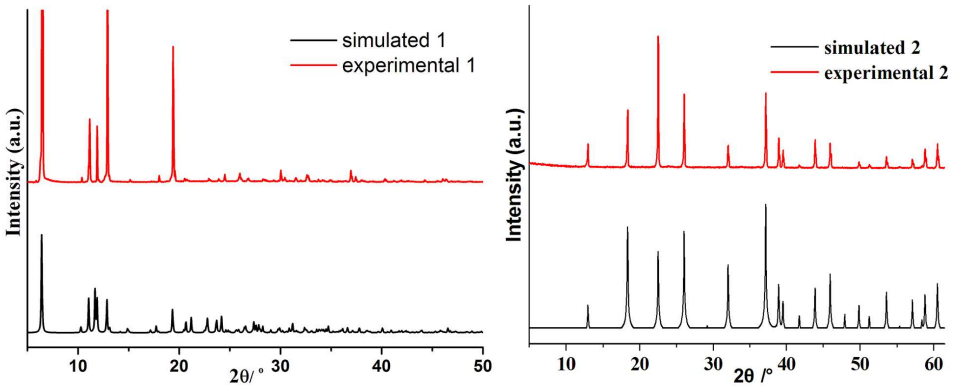

Figure S4. The experimental and simulated PXRD patterns of **1** and **2**.

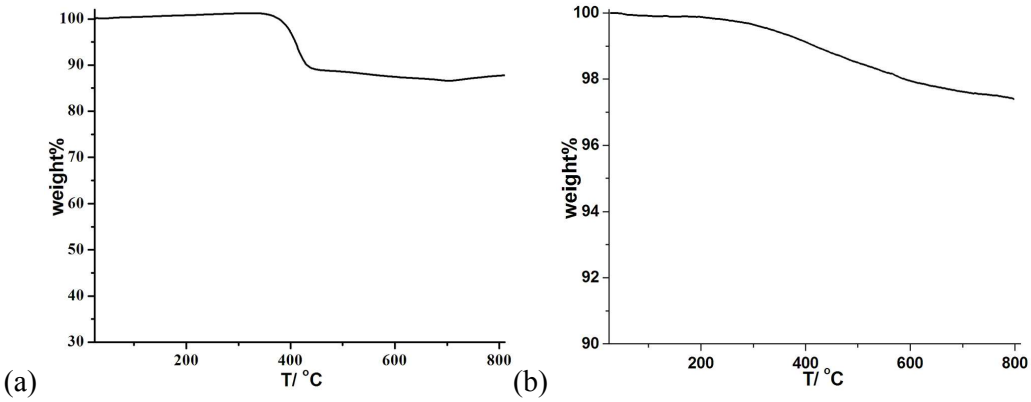

Figure S5. TG curves of compound **1** (a) and **2** (b) under air atmosphere (10 ºC/min).

The curves shows that the compound **1** and **2** remains stable up to 330 ºC and 160ºC, respectively. On further heating, a gradual weight loss of 13.2% and 2.57% were observed for **1** (calcd 13.6%) and **2** (calcd 3.07%), which are assigned to the removal of organic templates and OH groups for **1** and OH groups for **2**, respectively.

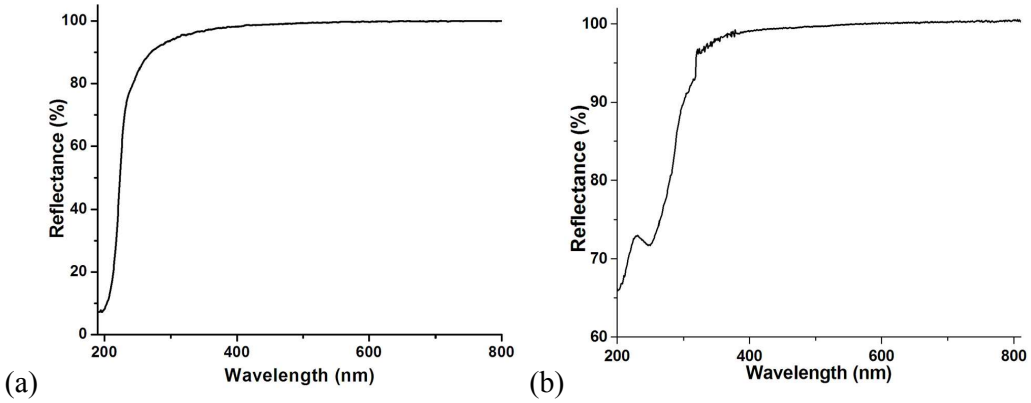

Figure S6. UV−vis diffuse reflectance spectrum of **1-2**.

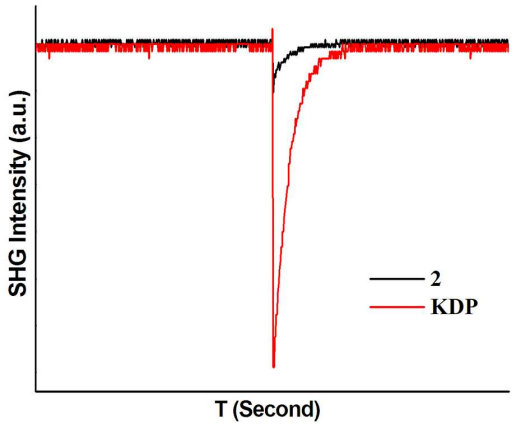

Figure S7. The SHG signals of **2** and KDP.

SHG measurement was performed on ground crystals of **2** using the Kurtz−Perry method. 1064 nm radiation was used as the fundamental frequency light while the SHG wavelength was 532 nm.

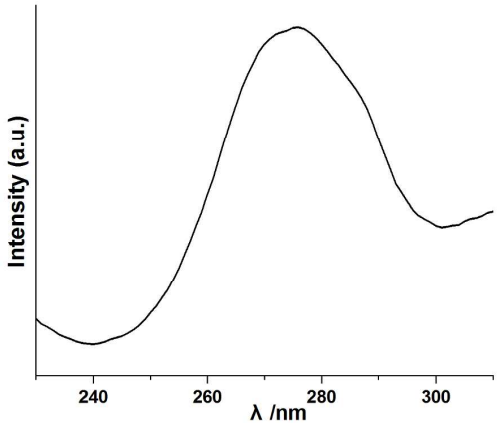

Figure S8. The excitation spectra of **2** in solid state at room temperature.