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ARTICLE TYPE

Incorporating $[GaB_4O_{11}(OH)]^{8-}$ clusters to construct luminescent galloborate with open-framework layers

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Hydrothermal reactions of $NH_4B_5O_8{\cdot}H_2O$, $BaCO_3$ and ethylenediamine lead to a new borate, namely, $Ba_2B_{10}O_{16}(OH)_2{\cdot}(H_3BO_3)(H_2O)$ (**1**). Compound **1** crystallizes in the triclinic space group *P*-1. Its structures features a 2D layered-structure constructed by $B_5O_{10}(OH)$ clusters. By further adding Ga_2O_3 into the reaction system, a new galloborate, namely, $BaGa(B_4O_8)(OH){\cdot}(H_2O)$ (**2**) was obtained. Compound **2** crystallizes in triclinic space group *P*-1. Its structure displays a rare 5-connected open-framework layers constructed by $GaB_4O_{11}(OH)$ units, which show nine membered ring (9-MR) channels within the layer and smaller 6MR transport-limiting openings perpendicular to the layer. The trigonal bipyramidal GaO_5 played a critical role in the formation of compound **2**. Interestingly, Compound **2** displays a blue luminescence.

Introduction

The search for crystalline inorganic layered solids are of great interest for their applications in intercalation reactions, ion-exchange and adsorption processes due to their chemically manipulable features within the interlamellar region.[1-5] Among these reported layered materials, three-dimensionally (3D) microporous layered structure is expected to possess unique properties, owing to the existence of micropores both parallel and perpendicular to the layers. Up to now, only several examples of 3D microporous layers have been reported in silicates,[6-7] and borogermanate.[8] For example, an aluminosilicate (denoted as MCM-22P) has large pores running within the layer and smaller six membered rings (6MR) transport-limiting openings perpendicular to the layer,[6] the microporous MCM-22P can be used as precursor to obtain mesoporous materials *via* pillaring or delamination processes.[9-10] Tsapatsis and co-workers reported a layered silicate (denoted as AMH-3), which contain 8MR pores along the thickness of the silicate layer as well as within the layers, AMH-3 show good thermal and acid stability.[7] Zhao and co-workers prepared a 3D open-framework layerd borogermanate, which show intersecting 8MR and 9MR apertures constructed by $B_4O_8(OH)$ and Ge_2O_7 units.[8]

Boron atoms can be three- and four-coordinated to O atoms to form various polyborate cluster-building units from $[B_3O_3(OH)_4]^-$ to $[B_{18}O_{36}]^{18-}$.[11-13] The combination of these B-O clusters with tetrahedral AlO_4 afford a series of open-framework aluminoborates under hydro/solvothermal conditions.[14] In these open-framework aluminoborates, Al^{3+} ions usually exhibit tetrahedral coordination geometry. Compared with Al^{3+} ion, Ga^{3+} has a similar outer electronic configuration and larger ionic radii, which may adopt different coordination geometries, such as square pyramid, trigonal bipyramida, and octahedron.[15] In addition, inorganic open-framework materials usually exhibit interesting luminescence properties such as single component white light emitting phosphors.[16] Therefore, it is interesting to introduce Ga^{3+} ions into borate backbones to obtain the luminescent open-framework galloborates.

Previous studies mainly use the high temperature solid-state method to obtain new galloborate materials.[15,17] In contrast, the synthesis of galloborates under middle-temperature hydrothermal conditions is still less explored.[18] Herein, we report the syntheses, structures and properties of two new metal borates: $Ba_2B_{10}O_{16}(OH)_2{\cdot}(H_3BO_3)(H_2O)$ (**1**) and $BaGa(B_4O_8)(OH){\cdot}(H_2O)$ (**2**). Colorless lamellar crystals of **1** were obtained by hydrothermal reactions of $NH_4B_5O_8{\cdot}H_2O$, $BaCO_3$ and ethylenediamine in water at 170 °C for 6 days, while lamellar crystals of **2** were obtained by further adding Ga_2O_3 into the reaction system. It should be stressed that **1-2** could not be obtained in the absence of ethylenediamine, which presumably adjust the pH values of the reaction systems.

Experimental

Materials and methods

Table 1. Crystal Data and Structure Refinement for Compounds **1-2**

	1	**2**
formula	$Ba_2B_{11}H_7O_{22}$	$BaB_4GaH_3O_{10}$
CSD number	427176	427177
M_r	752.65	413.32
crystal system	triclinic	triclinic
space group	*P*-1	*P*-1
a (Å)	6.7745(11)	7.1080(14)
b (Å)	6.8452(16)	7.1372(12)
c (Å)	21.531(4)	9.878(3)
α (deg)	88.152(16)	106.885(17)
β (deg)	82.974(12)	91.569(17)
γ (deg)	60.518(9)	119.185(11)
V (Å^3)	862.2(3)	410.00(15)
Z	2	2
D_c (g cm^{-3})	2.899	3.348
F(000)	700	380
GOF	1.025	1.154
collected reflns	12671	5706
unique reflns (R_{int})	3901 (0.0356)	1828 (0.0517)
observed reflns [$I > 2\sigma(I)$]	3253	1505
$R_1{}^a/wR_2{}^b$ [$I > 2\sigma(I)$]	0.0261/ 0.0554	0.0324 / 0.0651
$R_1{}^a/wR_2{}^b$ (all data)	0.0364/ 0.0604	0.0479/ 0.0866

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $^bwR_2 = \{\Sigma[w(F_o{}^2-F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

All chemicals were purchased commercially and used without further purification. The Fourier transform infrared (FT-IR) spectra (KBr pellets) were recorded on an Nicolet NEXUS670 spectrometer. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C analyzer with a heating rate of 10 °C/min under an air atmosphere. Powder X-ray diffraction (XRD) data were obtained using a Philips PW3040/60 diffractometer with Cu-Kα radiation (λ = 1.54056 Å). Photoluminescence analyses were performed on an Edinburgh Instrument FLS920 fluorescence spectrometer.

Syntheses of the title compounds

$Ba_2B_{10}O_{16}(OH)_2\cdot(H_3BO_3)(H_2O)$ (**1**). A mixture of $NH_4B_5O_8\cdot H_2O$ (2 mmol, 0.5444g), $BaCO_3$ (0.5 mmol, 0.0987g), ethylenediamine (0.5 mL), and H_2O (6 mL) (pHs = 10) was sealed in a 30 mL Telfon-lined bomb at 170 °C for 6 days and then slowly cooled to room temperature. Colorless lamellar crystals of **1** were obtained (yield: 18% based on $BaCO_3$). IR bands (cm^{-1}) for **1**: 3470(vs), 3346(w), 3194(w), 1376(s), 1253(m), 1118(w), 1059(s), 972(s), 924(s), 819(m), 766(w), 707(w), 625(w).

$BaGa(B_4O_8)(OH)\cdot(H_2O)$ (**2**). A mixture of $NH_4B_5O_8\cdot H_2O$ (0.5 mmol, 0.1361g), $BaCO_3$ (0.5 mmol, 0.0987g), Ga_2O_3 (0.5 mmol, 0.0937g), ethylenediamine (0.5 mL), and H_2O (6 mL) (pHs = 12) was sealed in a 30 mL Telfon-lined bomb at 170 °C for 6 days and then slowly cooled to room temperature. Colorless lamellar crystals of **2** were obtained (yield: 33% based on $BaCO_3$). IR bands (cm^{-1}) for **2**: 3446(vs), 3241(m), 1411(s), 1311(w), 1229(s), 1042(m), 930(s), 854(w), 766(w), 742(w), 661(w).

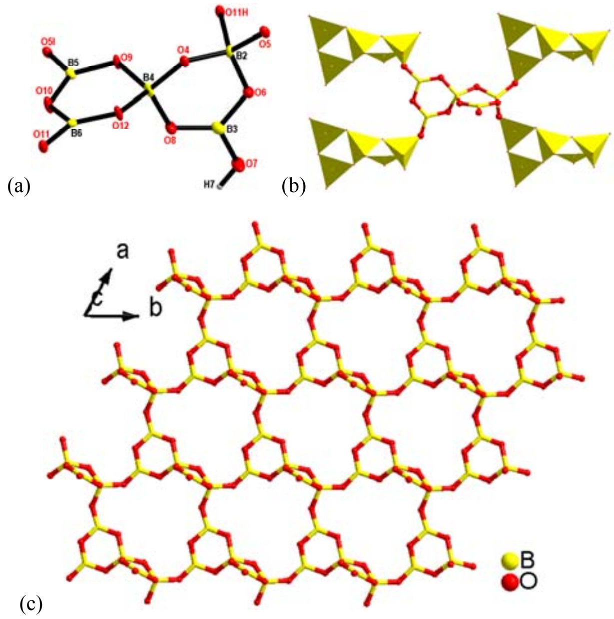

Figure 1. (a) one $B_5O_{10}(OH)$ cluster in **1**, Symmetry codes for the generated atoms are the same as those in Table 2. (b) View of the linkage of $B_5O_{10}(OH)$ cluster units in **1**. (c) View of the 2D B-O layer constructed by $B_5O_{10}(OH)$ clusters with nine-membered boron-ring windows.

The experimental powder X-ray diffraction (PXRD) patterns of compounds **1–2** correspond well with the simulated PXRD patterns of **1–2**, the difference in reflection intensities between the simulated and experimental patterns was due to the variation in the preferred orientation of the powder sample during collection of the experimental PXRD data (Figure S1).

Single-crystal structure determination

The intensity data were collected on a Bruker APEX II (**1-2**) with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at

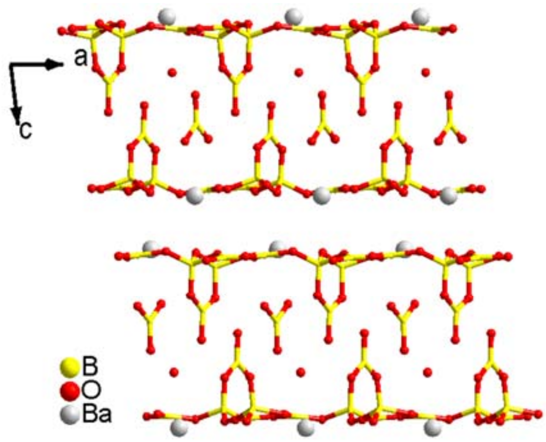

Figure 2. View of the packing structure of **1** along the *b* axis.

room temperature. All absorption corrections were performed using the multiscan program. The structures were solved by direct methods and refined by full-matrix least squares on F^2 with the SHELXTL-97 program.[19] All hydrogen atoms are located at geometrically calculated positions and refined with isotropic thermal parameters. All atoms except H atoms were refined anisotropically. Further details for structural **1-2** analyses are summarized in Table 1, selected bond lengths of compounds **1-2** are listed in Table 2, 3. More details on the crystallographic data are given in the CIF (see the Supporting Information).

Results and discussion

Structure of 1. Single-crystal X-ray analysis indicates that the asymmetric unit of compound 1 contains 35 independent non-H-atoms, including 2 Ba, 11 B and 22 O. The B atoms adopt two

Table 2. Selected bond lengths (Å) for compound **1**[a]

Ba(1)-O(9A)	2.635(3)	B(3)-O(7)	1.367(6)
Ba(1)-O(12)	2.637(3)	B(3)-O(6)	1.373(5)
Ba(1)-O(10B)	2.657(3)	B(4)-O(4)	1.450(5)
Ba(1)-O(1)	2.843(4)	B(4)-O(8)	1.477(6)
Ba(1)-O(3)	2.859(3)	B(4)-O(9)	1.481(5)
Ba(1)-O(4)	2.880(3)	B(4)-O(12)	1.493(5)
Ba(1)-O(4C)	2.909(3)	B(5)-O(9)	1.363(5)
Ba(1)-O(11B)	2.934(3)	B(5)-O(5I)	1.364(5)
Ba(1)-O(5D)	2.970(2)	B(5)-O(10)	1.369(5)
Ba(1)-O(5C)	2.983(3)	B(6)-O(12)	1.349(5)
Ba(1)-O(11E)	3.030(3)	B(6)-O(11)	1.357(5)
Ba(2)-OW1	2.623(3)	B(6)-O(10)	1.415(5)
Ba(2)-O(15A)	2.642(3)	B(7)-O(19D)	1.361(5)
Ba(2)-O(21)	2.659(3)	B(7)-O(21)	1.368(5)
Ba(2)-O(13B)	2.684(2)	B(7)-O(13)	1.372(5)
Ba(2)-O(20F)	2.848(3)	B(8)-O(15)	1.350(5)
Ba(2)-O(20A)	2.883(3)	B(8)-O(14)	1.360(5)
Ba(2)-O(14B)	2.950(2)	B(8)-O(13)	1.416(5)
Ba(2)-O(19D)	2.978(3)	B(9)-O(20)	1.442(5)
Ba(2)-O(14G)	2.993(3)	B(9)-O(16)	1.453(5)
Ba(2)-O(19F)	3.021(3)	B(9)-O(21)	1.496(5)
B(1)-O(1)	1.348(6)	B(9)-O(15)	1.509(5)
B(1)-O(2)	1.352(6)	B(10)-O(17)	1.364(6)
B(1)-O(3)	1.354(6)	B(10)-O(18)	1.369(6)
B(2)-O(6)	1.458(5)	B(10)-O(16)	1.373(5)
B(2)-O(4)	1.469(5)	B(11)-O(18)	1.451(5)
B(2)-O(5)	1.494(5)	B(11)-O(20)	1.478(5)
B(2)-O(11H)	1.513(5)	B(11)-O(19)	1.490(5)
B(3)-O(8)	1.362(6)	B(11)-O(14B)	1.515(5)

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

coordination models of BO_3 triangle (B1, B3, B5, B6, B7, B8 and B10) and BO_4 tetrahedron (B2, B4, B9 and B11). The B-O bond distances vary from 1.348(6) to 1.416(5) Å for the BO_3 triangles (Δ) and from 1.442(5) to 1.515(5) Å for the BO_4 tetrahedra (T) (Table 2). Three BO_3 triangles and two BO_4 tetrahedra are linked *via* bridging O atoms to form the $B_5O_{10}(OH)$ unit containing two planar B_3O_3 rings, which are almost perpendicular to each other (Figure 1a, S2). The $B_5O_{10}(OH)$ cluster can be written as (5:3Δ + 2T), which is different from the known penta-borate cluster units of B_5O_{10} (5:4Δ +T),[14a] and B_5O_{12} (5:2Δ + 3T).[11e] Each $B_5O_{10}(OH)$ cluster connects with four neighboring others by corner-sharing O atoms to form a 2D-layered structure with 9MR in the *ab* plane (Figure 1b,1c). The hydroxyls of the $BO_2(OH)$ triangles of each layer point into the same sides with the same orientations. Ba^{2+} ions are located in the cavity of the nine-membered boron rings within the layer, while guest water and H_3BO_3 molecules are located between two adjacent layers (Figure 2). The 10- and 11-coordinate Ba-O bond distances vary from 2.623(3) to 3.021(3) Å and from 2.635(3) to 3.030(3) Å, respectively. There are weak H-bonding interactions between adjacent layers. Bond valence sum (BVS) calculations gave total bond valences of 1.25, 1.03, 1.26, 1.00, 1.02 and 0.39 for O1, O2, O3, O7, O17 and OW1, respectively, indicating that O1, O2, O3, O7 and O17 are OH group; other O, Ba and B atoms are in an oxidation state of -2, +2, +3, respectively.

Structure of 2. The asymmetric unit of **2** contains 16 independent non-H atoms, including one Ga, one Ba, four B, and ten O atoms. The Ga^{3+} ion is five-coordinate with a trigonal bipyramidal coordination geometry (Figure 3a). The Ga-O distances range from 1.862(4) to 2.057(4) Å. The B atoms adopt two kinds of coordination models, with B-O bond distances

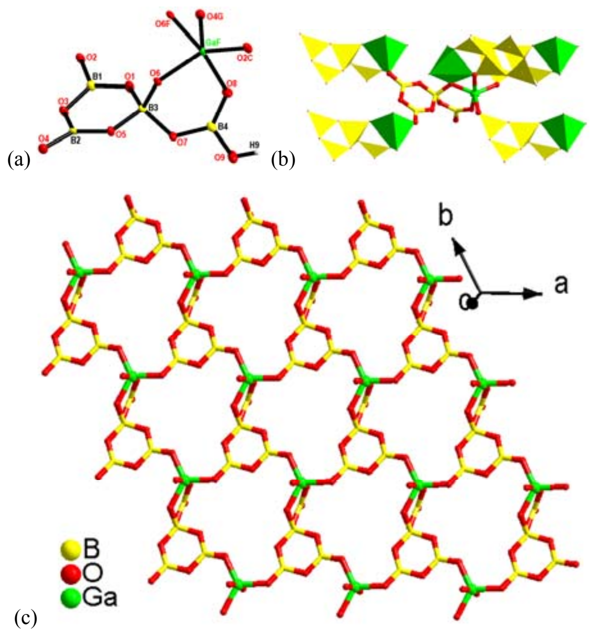

Figure 3. (a) $GaB_4O_{11}(OH)$ cluster in **2**, Symmetry codes for the generated atoms are the same as those in Table 3. (b) View of the linkage of $GaB_4O_{11}(OH)$ cluster units in **2**. (c) View of the the single sheet constructed by $GaB_4O_{11}(OH)$ clusters.

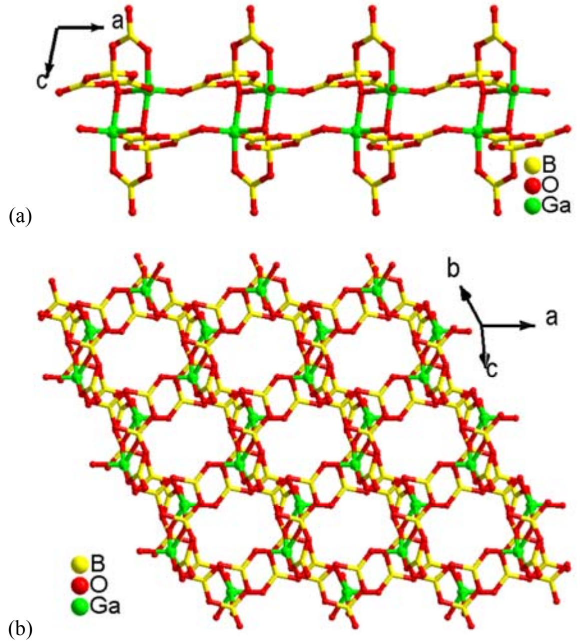

Figure 4. View of 6-MR along the thickness of the layer (a) as well as 9-MR pores within the layer (b) in **2**.

varying from 1.333(9) to 1.408(8) Å for the BO_3 triangles (B1, B2 and B4) and from 1.462(8) to 1.471(8) Å for the BO_4 tetrahedra (B3) (Table 3). Three BO_3 triangles and one BO_4 tetrahedra are linked *via* bridging O atoms to give a $B_4O_8(OH)$ unit containing one B_3O_3 ring and one attached BO_3 triangle (Figure 3a). BVS calculations gave total bond valences of 1.21 and 0.30 for O9 and OW1, indicating that O9 is an OH group; other O, Ba, Ga, and B atoms are in oxidation states of -2, +2, +3, and +3, respectively. The $B_4O_8(OH)$ unit chelates a trigonal bipyramidal GaO_5 center through μ_2-O8 and μ_3-O6 atoms,

Table 3. Selected bond lengths (Å) for compounds **2**[a]

Ba-OW1	2.717(6)	Ga-O(6)	2.057(4)
Ba-O(9A)	2.771(5)	B(1)-O(2)	1.355(9)
Ba-O(2B)	2.774(4)	B(1)-O(1)	1.369(8)
Ba-O(5)	2.826(4)	B(1)-O(3)	1.399(9)
Ba-O(1B)	2.850(5)	B(2)-O(4)	1.351(9)
Ba-O(4C)	2.920(4)	B(2)-O(5)	1.356(7)
Ba-O(6)	2.934(5)	B(2)-O(3)	1.408(8)
Ba-O(4D)	2.934(5)	B(3)-O(1)	1.462(8)
Ba-O(3C)	2.970(4)	B(3)-O(7)	1.468(8)
Ba-O(7)	3.069(5)	B(3)-O(5)	1.470(9)
Ga-O(2E)	1.862(4)	B(3)-O(6)	1.471(8)
Ga-O(4D)	1.877(5)	B(4)-O(8)	1.333(9)
Ga-O(6F)	1.887(4)	B(4)-O(9)	1.386(9)
Ga-O(8F)	1.951(5)	B(4)-O(7)	1.391(9)

[a]Symmetry codes for **1**: (A) $-x+1, -y+2, -z+2$; (B) $x+1, y, z$; (C) $x, y-1, z$; (D) $-x+1, -y+2, -z+1$; (E) $-x, -y+2, -z+1$; (F) $-x, -y+1, -z+1$; (G) $x-1, y-1, z$.

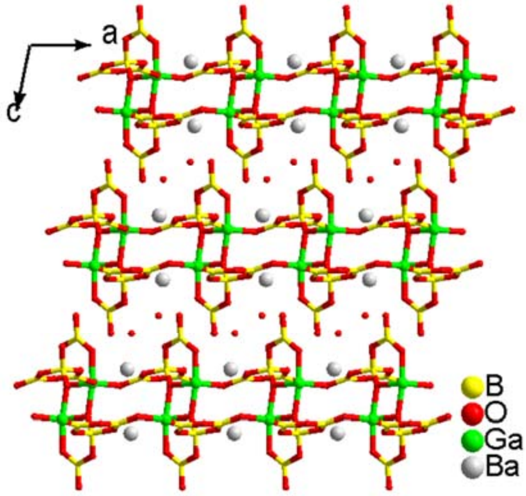

Figure 5. View of the packing structure of **2** along the *b* axis.

forming a novel $GaB_4O_{11}(OH)$ cluster. The $GaB_4O_{11}(OH)$ cluster can be considered as a tetrahedral BO_4 in $B_5O_{10}(OH)$ replaced by a trigonal bipyramidal GaO_5. Each $GaB_4O_{11}(OH)$ cluster linked to four nearest neighbors by bridging O2 and O4 atoms, giving rise to an galloborate sheet in the *ab* plane with 9-MR windows, which is built from three GaO_5 trigonal bipyramida, two BO_4 tetrahedra and four BO_3 triangles with a diameter of 6.9 Å×6.9Å (Figure 3b,3c). The two adjacent layers are further linked by Ga-O bonds to give a porous layers with a thickness of 10.3 Å, the layers contain 9-MR channels within the layer and smaller 6MR transport-limiting openings perpendicular to the layer (Figures 4a,4b). The charge balancing Ba^{2+} cations and water molecules are located in the interlayer space (Figures 5). Such 3D porous layers are of particular interest because they open up the possibility of a route towards combined microporous–mesoporous materials. The OH groups (O9) of open-framework layers point to the interlayer space, which makes it impossible for the adjacent layers to further extend to 3D frameworks by dehydrated condensation of the OH groups. From the topological point of view, the framework of **2** can be reduced into a rare 5-connected net with a Schläfli symbol of $(4^8 6^2)$, in which $GaB_4O_{11}(OH)$ clusters act as 5-connected nodes (Figure 6). To date, 5-connected nets are extremely rare in inorganic solids and metal-organic frameworks,[20] the framework reported herein defines a new topology for 5-connected networks to the best of our knowledge. In addition, the unique linkage mode of $GaB_4O_{11}(OH)$ clusters is also different to the known 3D microporous layered structures in silicates and borogermanate.[6-8]

Thermogravimetric analyses (TGA)

The thermal behavior of **1** and **2** were examined by TG analysis in dry air atmosphere from 30 to 800 °C. These compounds show a similar thermal behavior and undergo one step of weight loss. The weight loss above 150 °C is due to the decomposition and collapse of the whole frameworks (calcd/found, 8.38/8.51% for **1**; calcd/found, 6.54/6.48% for **2**; Figure S3).

Optical spectroscopy

Compounds **1-2** show similar IR spectra. In the IR spectra of **1**,

(a)

(b)

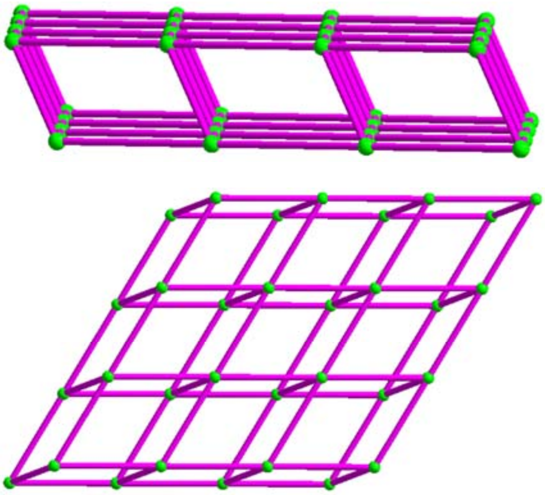

Figure 6. (a)/(b) View of the topology network in **2**, in which the $GaB_4O_{11}(OH)$ clusters are shown as green nodes.

the strong and broad absorption bands in the range of 3000−3700 cm^{-1} are assigned as characteristic peaks of OH vibration. The characteristic band around 1360-1220 cm^{-1} is due to the B-O asymmetric stretching of BO_3 units. The band around 1000 cm^{-1} is associated with BO_4 units (Figure S4). Compound **2** emits intense blue luminescence and exhibits strong emissions around 437 nm when excited at 370 nm. (Figure 7, S5), the decay lifetime is 2.95 ns. The blue emissions of compound **2** are similar to the recently reported luminescent borates.[14a,16c] The luminescent mechanism may attributed to the presence of various kinds of lattice defects.[21]

Conclusions

In summary, two new layered borates have been successfully made by incorporating cluster building units under hydro-thermal

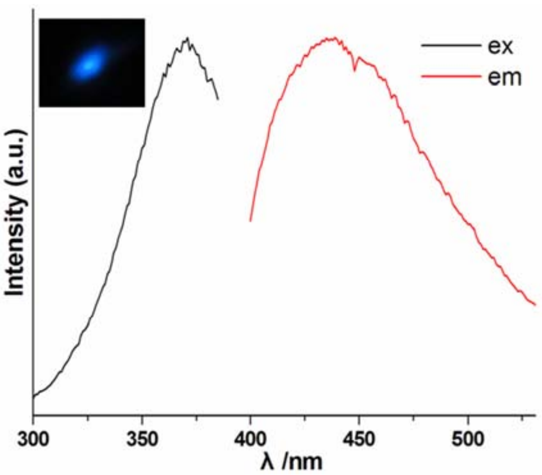

Figure 7. Emission spectra of **2** (ex = 370 nm) in solid state at room temperature. The inset showing optical luminescence image of the solid samples.

conditions. Compound **1** features a 2D-layered structure in which $B_5O_{10}(OH)$ clusters are bridged by corner-sharing O atoms. By further adding Ga_2O_3 into the reaction system, a luminescent galloborate consist of $GaB_4O_{11}(OH)$ clusters was obtained, which display a rare 5-connected open-framework layers with intersecting 9MR and 6MR pores within the layers and along the thickness of the layer. The trigonal bipyramidal GaO_5 played a critical role in the formation of compound 2, in which the adjacent layers are linked through one O atom of GaO_5 in the axial position. Further work is in progress for discovering new galloborates under hydrothermal conditions.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Additional characterizing data. CSD reference numbers 427176 and 427177. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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TOC:

Incorporating $[GaB_4O_{11}(OH)]^{8-}$ clusters to construct luminescent galloborate with open-framework layers

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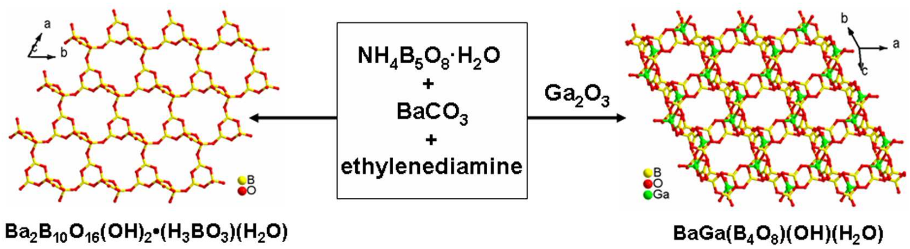

A luminescent 5-connected galloborate with open-framework layers has been obtained under mild hydrothermal conditions by incorporating $[GaB_4O_{11}(OH)]^{8-}$ clusters