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**Mullite-type Ga$_4$B$_2$O$_9$: structure and order-disorder phenomenon**

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Supporting information:

**Figure S1** SEM image of Ga$_4$B$_2$O$_9$ synthesized by solid state reaction.

**Figure S2** X-ray diffraction patterns of the samples synthesized by (a) boric acid flux method; (b) solid state reaction at 600°C for 15 hours; (c) 650°C for 5 hours; (d) 650°C for 15 hours; and (e) 700°C for 5 hours.

**Figure S3** Rietveld plot of the powder X-ray diffraction pattern of Ga$_4$B$_2$O$_9$ using the ordered model.

**Structure analysis for Al$_{16}$B$_6$Si$_2$O$_{37}$**

The structure of Al$_{16}$B$_6$Si$_2$O$_{37}$ is related to that of Al$_4$B$_2$O$_9$, as shown in Figure S4, whose inter-chain units include Si$_2$O$_7$ dimmers, edge-sharing AlO$_5$ trigonal bipyramids trimers and dimers, BO$_3$ and BO$_4$ groups (Peacor et al., 1999). The fundamental building units are defined by structure deconstruction analysis, including BU-, S, B$_5$, B$_6$, T$_3$, T$_4$, D and E, as shown in Figure S5. The main structure is ordered, except the partially occupied O10A and O10B atoms. These two sites are very close and constrained by the sum of the occupancies to 1 during the refinement. In the total four effective oxygen atom positions, the occupancies of O10A and O10B were 3.75 and 0.25 respectively. When O10A is occupied, the correlated inter-chain unit is a dimer formed by edge-sharing AlO$_5$ trigonal bipyramids.
When O10B is occupied, Al3 (partly substituted by B) is tetrahedrally coordinated, and the coordination of B2 changes from tetrahedron to trigonal plane. Since the occupancy of O10B is low and the disordered phenomenon does not influence the connectivity of BUs, the fully occupied O10A model is used in the structure analysis. Similar to the analysis of the structures of Ga4B2O9 and Al4B2O9, a single sheet perpendicular to the b-direction can be extracted and shown in Figure S6a, and its description by using BUs is shown in Figure S6b. Starting from the uniquely defined ET1DT2 chain along the [101] direction, D can only link to B6 and then to E, which leads to a uniquely defined chain DB6EB5D along the [10-1] direction. The extension of the chain starting from E should be EB5DB6E as shown in Figure S6b. Since the connections of D and E to T3 and T4 are all unidirectional, the other [10-1] chains consisting of A, S, T3 and T4 are also uniquely defined. Therefore, the 2D unit cell shown in Figure S6b reproduces the real cell of Al16B6Si2O37 nicely. The 3D structure can then be formed by stacking the ac-sheet along the b-axis (1/2b) with a shift of 1/2a. The connectivity of the building units in the structure of Al16B6Si2O37 is ordered.

**Figure S4** Projection of the structure of Al16B6Si2O37 along the b-direction.

**Figure S5** Fundamental building units in the structure of Al16B6Si2O37.

**Figure S6** (a) The mono-ac-sheet isolated from the structure of Al16B6Si2O37; (b) The ordered sheet in Al16B6Si2O37 constructed by fundamental building units.

![Figure S1. SEM image of Ga4B2O9 synthesized by solid state reaction.](image-url)
Figure S2. X-ray diffraction patterns of the samples synthesized by (a) boric acid flux method; (b) solid state reaction at 600°C for 15 hours; (c) 650°C for 5 hours; (d) 650°C for 15 hours; and (e) 700°C for 5 hours.

Figure S3. Rietveld plot of the powder X-ray diffraction pattern of Ga$_4$B$_2$O$_9$ using the ordered model.
Figure S4. Projection of the structure of Al₁₆B₆Si₂O₃₇ along the b-direction. (Red, pink, blue and light blue spheres represent Al, Si, B and O atoms, respectively; octahedra are AlO₆).

Figure S5. Fundamental building units in the structure of Al₁₆B₆Si₂O₃₇.

Figure S6. (a) The ac-sheet isolated from the structure of Al₁₆B₆Si₂O₃₇; (b) The ordered sheet in Al₁₆B₆Si₂O₃₇ constructed by fundamental building units.