KD5038 supporting

Mullite-type $Ga_4B_2O_9$: structure and order-disorder phenomenon

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Supporting information:

Figure S1 SEM image of $Ga_4B_2O_9$ 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 $Ga_4B_2O_9$ using the ordered model.

Structure analysis for $Al_{16}B_6Si_2O_{37}$

The structure of $Al_{16}B_6Si_2O_{37}$ is related to that of $Al_4B_2O_9$, as shown in Figure S4, whose inter-chain units include Si_2O_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-*A*, *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 $Al3O_5$ 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 $Ga_4B_2O_9$ and $Al_4B_2O_9$, 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 ET_1DT_2 chain along the [101] direction, *D* can only link to B_6 and then to *E*, which leads to a uniquely defined chain DB_6EB_5D along the [10-1] direction. The extension of the chain starting from *E* should be EB_5DB_6E as shown in Figure S6b. Since the connections of *D* and *E* to T_3 and T_4 are all unidirectional, the other [10-1] chains consisting of *A*, *S*, T_3 and T_4 are also uniquely defined. Therefore, the 2D unit cell shown in Figure S6b reproduces the real cell of $Al_{16}B_6Si_2O_{37}$ nicely. The 3D structure can then be formed by stacking the **ac**-sheet along the **b**-axis (1/2***b***) with a shift of 1/2***a***. The connectivity of the building units in the structure of $Al_{16}B_6Si_2O_{37}$ is ordered.

Figure S4 Projection of the structure of $Al_{16}B_6Si_2O_{37}$ along the **b**-direction.

Figure S5 Fundamental building units in the structure of $Al_{16}B_6Si_2O_{37}$.

Figure S6 (a) The mono-**ac**-sheet isolated from the structure of $Al_{16}B_6Si_2O_{37}$; (b) The ordered sheet in $Al_{16}B_6Si_2O_{37}$ constructed by fundamental building units.

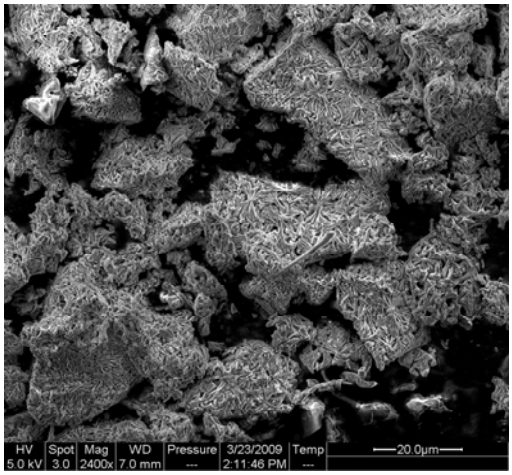

Figure S1. SEM image of $Ga_4B_2O_9$ synthesized by solid state reaction.

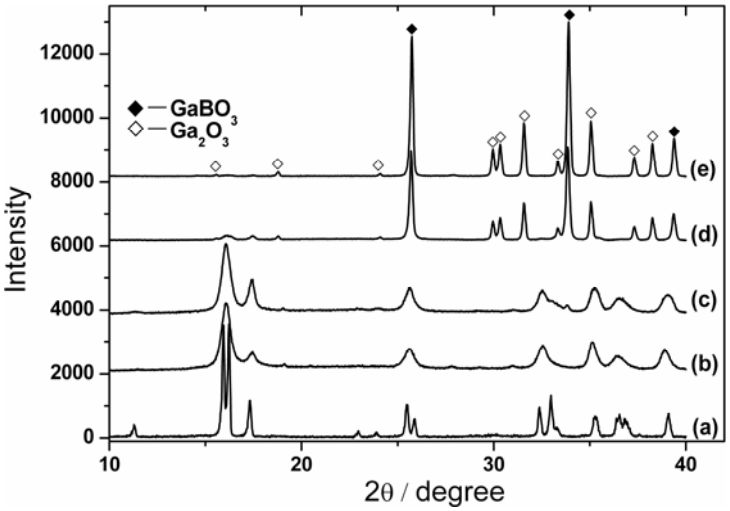

Figure S2. X-ray diffraction patterns of the samples synthesized by (a) boric acid flux method; (b) solid state reaction at 600°C for 15 hours; (c) 650°C for 5 hours; (d) 650°C for 15 hours; and (e) 700°C for 5 hours.

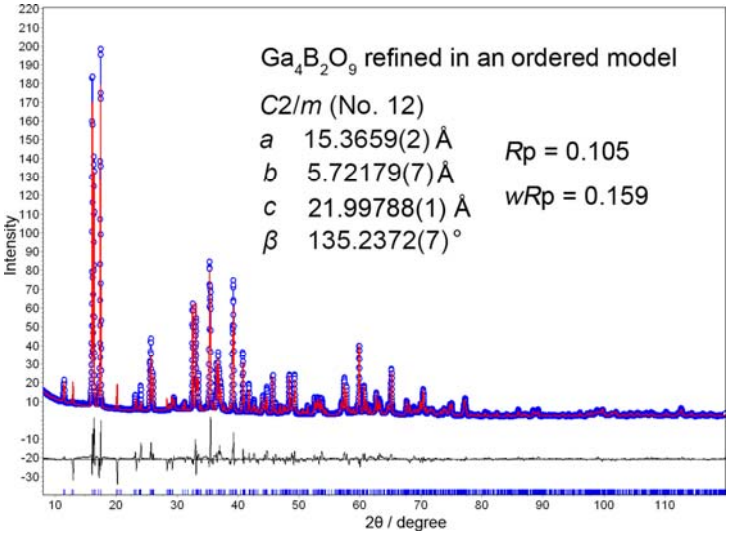

Figure S3. Rietveld plot of the powder X-ray diffraction pattern of $Ga_4B_2O_9$ using the ordered model.

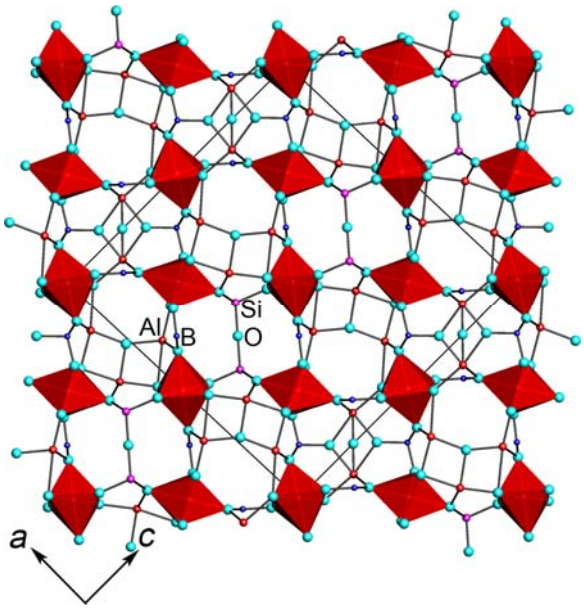

Figure S4. Projection of the structure of $Al_{16}B_6Si_2O_{37}$ along the **b**-direction. (Red, pink, blue and light blue spheres represent Al, Si, B and O atoms, respectively; octahedra are AlO_6).

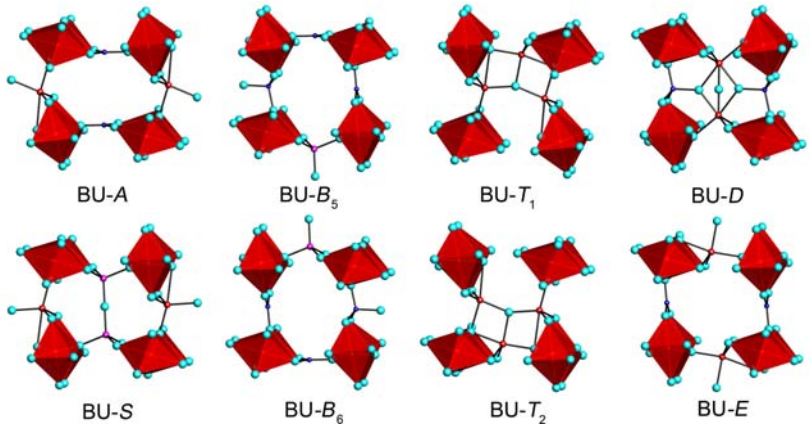

Figure S5. Fundamental building units in the structure of $Al_{16}B_6Si_2O_{37}$.

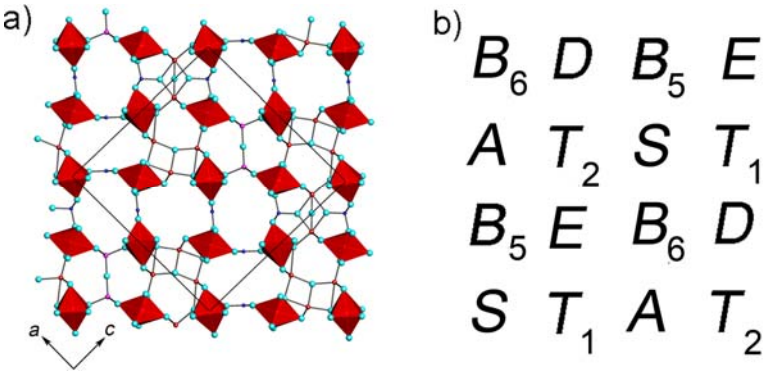

Figure S6. (a) The **ac**-sheet isolated from the structure of $Al_{16}B_6Si_2O_{37}$; (b) The ordered sheet in $Al_{16}B_6Si_2O_{37}$ constructed by fundamental building units.