

Supplementary Information

First-order phase transition in the $\text{Li}_2\text{B}_{12}\text{H}_{12}$ system

Mark Paskevicius,^a Mark P. Pitt,^a David H. Brown,^b Drew A. Sheppard,^a Somwan Chumphongphan,^a and Craig E. Buckley^a*

^a Department of Imaging and Applied Physics, Fuels and Energy Technology Institute, Curtin University, GPO Box U1987, Perth 6845, WA, Australia.

^b Department of Chemistry, Curtin University, Kent Street, Bentley 6102 WA, Australia.

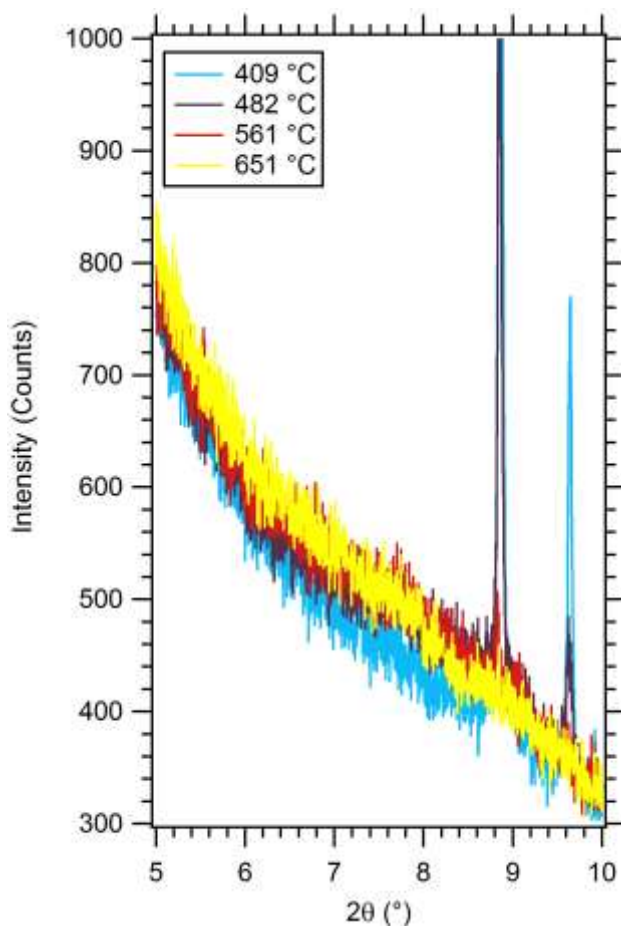


Figure S1. In-situ synchrotron XRD data ($\lambda = 1.000026 \text{ \AA}$) for the thermal decomposition of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ under vacuum. At high temperature the crystalline $\beta\text{-Li}_2\text{B}_{12}\text{H}_{12}$ polymorph transitions into a phase that diffracts with a broad halo that moves to higher d -spacing with increasing temperature. The halo is difficult to resolve due to significant attenuation from the sapphire capillary used to contain the sample. More pronounced diffraction halos can be observed in ex-situ data.^{S1}

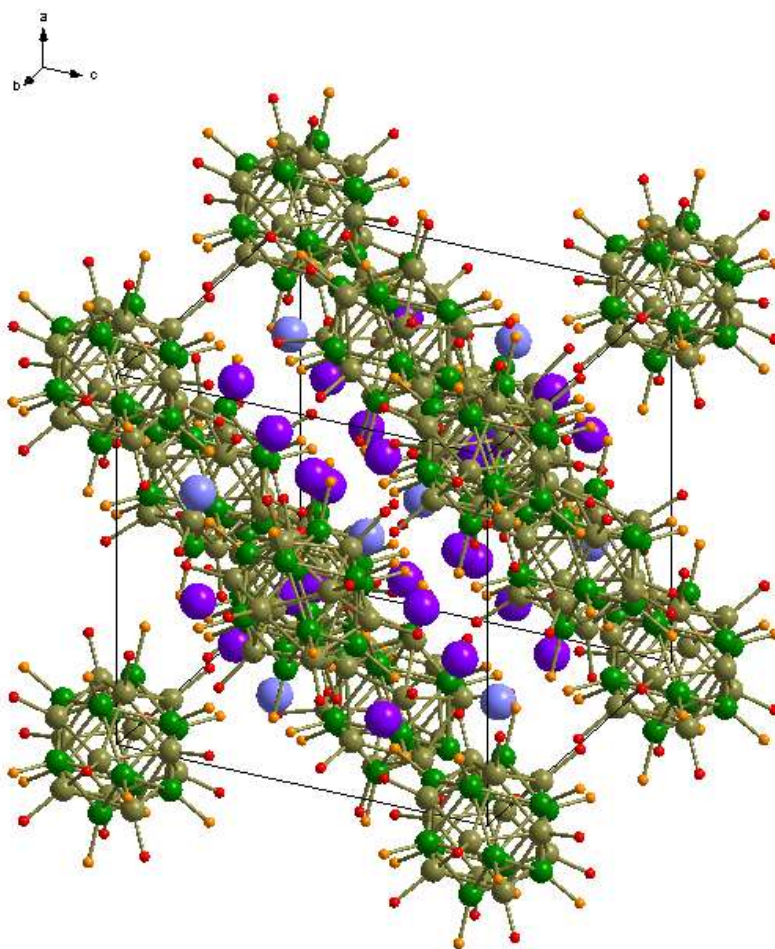


Figure S2. Average crystal structure of disordered β -Li₂B₁₂H₁₂. Olive atoms represent the original B icosahedra from the static pre transition structure. H atoms associated with the original static B₁₂H₁₂²⁻ anion are coloured red. The second rotated B icosahedron is represented by dark green atoms, with orange H atoms. Light blue atoms represent Li on the 8*c* position and purple atoms represent Li on 24*d*.

Table S1. Average structural coordinates of disordered β -Li₂B₁₂H₁₂. Space group *Pa*-3. Unit cell $a = 10.0172$ Å. Uncertainties for atomic coordinates are not provided as atoms were manually located to preserve the icosahedral shape, based partially on previous studies.^{S2-S3}

Atom	Wykoff	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy
Li	8 <i>c</i>	0.64620	0.64620	0.64620	0.2500
Li	24 <i>d</i>	0.35380	0.35380	0.64620	0.2500
B	24 <i>d</i>	-0.08722	-0.08700	0.11817	0.5000
B	24 <i>d</i>	-0.03438	-0.03716	-0.16303	0.5000
H	24 <i>d</i>	-0.14996	-0.14958	0.20317	0.5000
H	24 <i>d</i>	-0.05910	-0.06389	-0.28029	0.5000
B	24 <i>d</i>	0.00000	-0.14521	0.08975	0.5000
B	24 <i>d</i>	0.00000	0.14521	0.08975	0.5000
H	24 <i>d</i>	0.00000	-0.24966	0.15430	0.5000
H	24 <i>d</i>	0.00000	0.24966	0.15430	0.5000

The β -Li₂B₁₂H₁₂ crystal structure was modeled by first starting with the α -Li₂B₁₂H₁₂ space group, *Pa*-3. A second B₁₂H₁₂²⁻ motif was added to the unit cell to approximate rotational disorder as described in a previous study on Cs₂B₁₂H₁₂.^{S3} Both B₁₂H₁₂²⁻ motifs are centered on the same sites in the unit cell but are rotated relative to each other, governed by the space group symmetry. The final structure maintains a boron icosahedron radius of 1.71 Å and an ideal B-H distance of 1.23 Å. Any further subtle refinement of the atomic coordinates will require neutron diffraction data.

References

- S1. Pitt, M. P.; Paskevicius, M.; Brown, D. H.; Sheppard, D. A.; Buckley, C. E. Thermal Stability of Li₂B₁₂H₁₂ and its Role in the Decomposition of LiBH₄. *J. Am. Chem. Soc.* **2013**, *135*, 6930-6941.
- S2. Her, J.-H.; Yousufuddin, M.; Zhou, W.; Jalisatgi, S. S.; Kulleck, J. G.; Zan, J. A.; Hwang, S.-J.; Bowman Jr., R. C.; Udovic, T. J. Crystal Structure of Li₂B₁₂H₁₂: a Possible Intermediate Species in the Decomposition of LiBH₄. *Inorg. Chem.* **2008**, *47*, 9757-9759.
- S3. Verdal, N.; Wu, H.; Udovic, T. J.; Stavila, V.; Zhou, W.; Rush, J. J. Evidence of a transition to reorientational disorder in the cubic alkali-metal dodecahydro-*closo*-dodecaborates. *J. Solid State Chem.* **2011**, *184*, 3110-3116.