Communication

First-order phase transition in the $Li_2B_{12}H_{12}$ system

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The thermal decomposition of anhydrous *Pa*-3 $Li_2B_{12}H_{12}$ was studied *in-situ* by high resolution synchrotron X-ray diffraction. A first-order phase transition can be observed at 355°C where the unit cell volume expands by ca. 8.7%. The

10 expanded β-$Li_2B_{12}H_{12}$ polymorph simultaneously decomposes to a hydrogen poor γ-$Li_2B_{12}H_{12-x}$ phase. Expansion of the unit cell across the discontinuity is consistent with reorientational motion of $B_{12}H_{12}^{2-}$ anions, and the presence of a frustrated Li^+ lattice indicating Li ion conduction.

15   With intrinsically high gravimetric and volumetric density, metal-hydrogen phases containing boron are appealing as potential hydrogen (H) stores for off-grid and vehicular applications, and are able to compete with Li batteries and diesel fuels on a cost and energy density basis.[1,2] In particular, the group

20 I and II metal-borohydrides such as $LiBH_4$ and $Mg(BH_4)_2$ are of great interest, containing 18.5 and 14.9 wt.% H respectively. Due to the current inability to find a temperature lowering catalytic additive, such phases must operate at temperatures higher than their melting points (T_m). For $LiBH_4$, this results in the generation

25 of the dodecahydro-*closo*-dodecaborate $Li_2B_{12}H_{12}$.[3-5] The $Li_2B_{12}H_{12}$ phase was found to decompose to a nanoscopic hydrogen-poor polymorph γ-$Li_2B_{12}H_{12-x}$. A new β-$Li_2B_{12}H_{12}$ polymorph was also discovered by ageing α-$Li_2B_{12}H_{12}$ (*Pa*-3 structure type[4]) at 450°C and 125 bar H_2 pressure.[3] The symmetry

30 of this new polymorph could not be identified due to a low yield and insufficient reflections for unit cell indexing. Attempts to quench high yields of the β-$Li_2B_{12}H_{12}$ polymorph to room temperature were unsuccessful.[3]

   Polymorphism in metal-borohydrides is abundant, for

35 example; $LiBH_4$ displays a first-order transition from an orthorhombic to a hexagonal structure at 108°C with an associated order-disorder transition of the BH_4^- units;[6,7] $Mg(BH_4)_2$ also displays an α/β transition at 180°C,[8] and a γ/ε transition at 150°C.[9] Polymorphism has also been observed in the

40 group I dodecahydro-*closo*-dodecaborates $M_2B_{12}H_{12}$ (*M* = K, Rb, Cs), with a second-order transition evident at 538°C, 469°C and 236°C respectively.[10] The entropic component of these second order transitions is characterised by rapid reorientational disordering of the icosahedral $B_{12}H_{12}^{2-}$ anion.[10] Although the

45 crystallographic coordination is preserved during these second-order transitions (e.g. the cations and $B_{12}H_{12}^{2-}$ icosahedral centres do not move from their original Wyckoff positions), a second $B_{12}H_{12}^{2-}$ motif is introduced into the structural model to describe

the average reorientational disordered structure of the $B_{12}H_{12}^{2-}$

50 anion.[10] This produces two anion positions with 50% occupancy to completely describe the crystal structure, indicating localised hopping/exchange of B and H atoms in the icosahedral $B_{12}H_{12}$ unit.

   The synthesis of anhydrous $Li_2B_{12}H_{12}$ from the hydrated form,

55 $Li_2B_{12}H_{12}.xH_2O$, has been described in detail in a previous study.[3] *In-situ* synchrotron X-ray diffraction (XRD) data on the thermal decomposition of $Li_2B_{12}H_{12}$ was collected on the Powder Diffraction Beamline at the Australian Synchrotron. Details regarding the diffractometer setup and intrinsic resolution have

60 been reported in previous work.[11] This study utilises a wavelength of $\lambda = 1.000026$ Å, with complete diffraction patterns collected every 1 minute, during temperature ramping of 5°C/minute under dynamic vacuum. The sample was sealed within a sapphire capillary (1 mm diameter, Crytur) to enable the

65 high temperature in-situ diffraction study. Temperature programmed desorption-mass spectroscopy (TPD-MS) of $Li_2B_{12}H_{12}$ was conducted at 2°C/minute under dynamic vacuum up to 630°C.
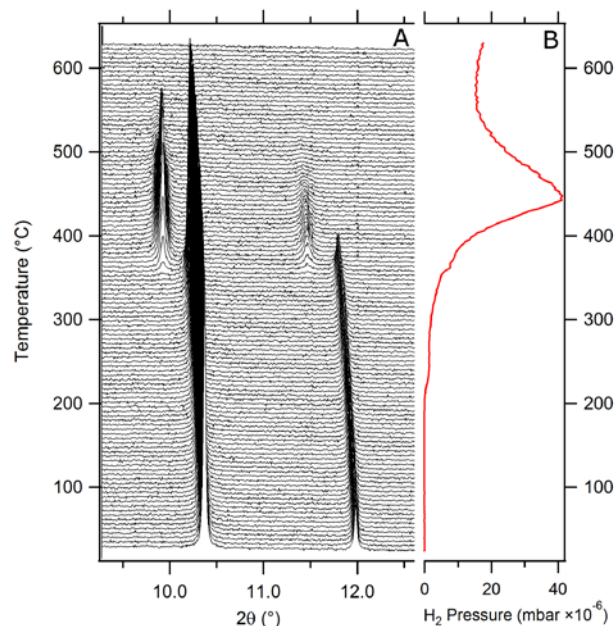

Figure 1. (a) In-situ synchrotron XRD data for the thermal

70 decomposition of $Li_2B_{12}H_{12}$ under vacuum up to 630°C. A select 2θ range over the main peaks is displayed. (b) TPD-MS of $Li_2B_{12}H_{12}$ under vacuum at 2°C/minute up to 630°C.

Fig. 1a shows the temperature dependent diffraction data from $Li_2B_{12}H_{12}$ up to 630°C. There is a clear shift in the reflections (111) and (200) at ca. 355°C. By ca. 550°C, no sharp crystalline reflections are evident, and only a broad halo remains (Figure S1), consistent with the release of H according to the TPD-MS in Fig. 1b. This broad halo is consistent with the H-poor γ-$Li_2B_{12}H_{12-x}$ observed in our previous study.[3] The H-poor γ-$Li_2B_{12}H_{12-x}$ phase is stable until ca. 650°C, when amorphous B can be observed to form.[3] Initial indexing of the post-step diffraction pattern revealed that the main (111) and (200) intensities were preserved with cubic unit cell symmetry. However, some higher angle reflections were quenched, becoming unobservable compared to their moderate intensities in the pre-step Pa-3 structure. This suggests that B and H atoms have moved off their static positions, consistent with reorientational disorder.

Fig. 2a shows the temperature dependent variation of the $Li_2B_{12}H_{12}$ lattice parameter, while Fig. 2b compares the diffraction patterns pre and post step. The unit cell volume is expanded by ca. 8.7% across the step. The discontinuous behaviour of the unit cell strongly indicates that a first-order phase transition has occurred. The fact that (111) and (200) remain in the post step β-$Li_2B_{12}H_{12}$ diffraction data indicates that the $B_{12}H_{12}^{2-}$ icosahedra retain a similar coordination to the pre-step Pa-3 environment, as the (111) planar spacing is indicative of the lateral spacing of $B_{12}H_{12}^{2-}$ icosahedral centres. Reflections such as (502) that are generated from B atoms within a $B_{12}H_{12}^{2-}$ icosahedral unit are strongly quenched post step. This quenching is consistent with the reorientational disordering of B and H positions that has been observed in second-order phase transitions in $Cs_2B_{12}H_{12}$.[10] Reflections such as (021) and (211) whose intensity is > 90% generated from Li^+ cations are also similarly quenched, suggesting that Li^+ cations are also undergoing a form of disordered motion. In this respect, the first-order polymorphic transition of $Li_2B_{12}H_{12}$ at ca. 355°C retains the same basic symmetry as the pre step Pa-3 structure, but with thermally induced disorder of the B, H and Li positions (hopping/exchange). Such a transformation is symmetry preserving, and may be regarded as a zero-order isosymmetric phase transition. It is notable that temperature induced zero-order isosymmetric phase transitions are extremely rare, and less than 10 phases are known to exhibit these properties.[12] Zero-order isosymmetric reactions are known to occur in framework structures with large coordination environments around cations.[12]

Utilising an averaged multiple icosahedra model,[10] we have included a second $B_{12}H_{12}^{2-}$ motif in the post step Pa-3 structure, with 50% occupancy of each B and H position. Further analysis of the Li^+ cation framework indicated that the Li partially migrated to a 24-fold (x, x, 1-x) Wykoff position (therefore quenching (021) and (211)), yielding a more symmetric distribution of Li, with an average 25% occupancy on each of the 8c and 24d positions. The multiple icosahedra/Li model reduces χ^2 from 1.677 to 1.592 and noticeably improves the fit to minor peaks. This suggests the Li^+ cations are constantly in motion on this disordered Li sublattice, implying that the β-$Li_2B_{12}H_{12}$ polymorph is a potential Li^+ superionic conductor. Such phases are well known in the tertiary Li containing hydrides,[13] and the $Li_2B_{12}H_{12}$ system may now offer a new and novel Li^+ ion conductor, whose transition temperature may be engineered through the addition of halides.
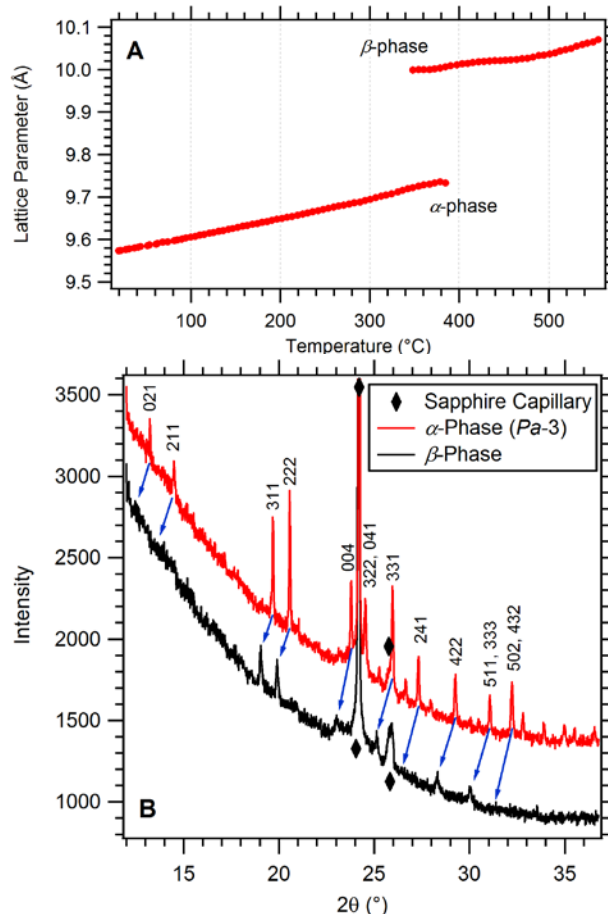

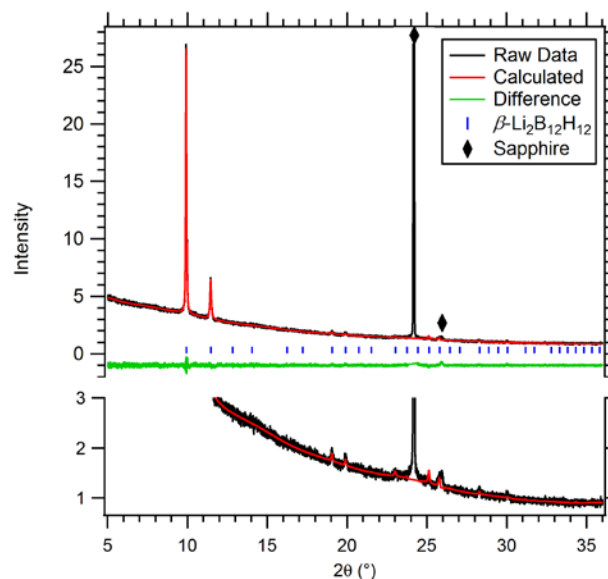**Figure 2.** (a) Temperature dependence of the unit cell. (b) Comparison of diffraction data pre and post step.

Figure 3. Rietveld refinement of the disordered Pa-3 structure type fitted to the post step β-$Li_2B_{12}H_{12}$ diffraction data. The lower figure is zoomed to show fit quality to weaker intensities.

Fig. 3 shows the Rietveld refinement of the disordered β-Li$_2$B$_{12}$H$_{12}$ polymorph. The structural details are shown in Figure S2 and Table S1. It should be noted that this is an average structural model that is conceptually similar to earlier work [10] based on neutron diffraction data of Cs$_2$B$_{12}$H$_{12}$. Due to the poor scattering from Li, B and H with X-rays, further research should be undertaken with neutrons to completely elucidate the structural model, although this would require isotopic ^{7}Li^{11}B$_{12}$D$_{12}$. The β-Li$_2$B$_{12}$H$_{12}$ polymorph exists over a wide temperature range, ca. 355 - 550°C, and during this period, significant H loss occurs from the sample, as observed from the TPD-MS in Fig. 1b. H loss through the transition at 355°C is minor, but after 400°C, significant H loss occurs, and the β-Li$_2$B$_{12}$H$_{12}$ polymorph decomposes directly to the nanocrystalline H-poor γ-Li$_2$B$_{12}$H$_{12-x}$ polymorph, which diffracts with a broad halo in the 5.85 - 7.00 Å d-spacing range, dependent on the amount of H released.[3]

The heavy group I dodecahydro-*closo*-dodecaborates M_2B$_{12}$H$_{12}$ (M = K, Rb, Cs) all reside in the *Fm*-3 space group at room temperature with cations occupying an 8c (0.25, 0.25, 0.25) site between B$_{12}$H$_{12}$$^{2-}$ anions. The space group symmetry is related to the cation size and both Na$_2$B$_{12}$H$_{12}$ (*P2$_1$/n*) and Li$_2$B$_{12}$H$_{12}$ (*Pa*-3) exist in different space groups at room temperature. For M_2B$_{12}$H$_{12}$ (M = K, Rb, Cs), the B$_{12}$H$_{12}$$^{2-}$ anion centre to cation distance is always large enough (> 4.6 Å) to ensure that even with a second B$_{12}$H$_{12}$$^{2-}$ motif, the minimum M-H distance is never violated. As such, the cation does not need to move due to shortened M-H separation, and a second order transition ensues. For disordered β-Li$_2$B$_{12}$H$_{12}$, the B$_{12}$H$_{12}$$^{2-}$ anion centre to Li$^+$ distance is significantly shorter (ca. 4.1 Å), and with a second B$_{12}$H$_{12}$$^{2-}$ motif, moderately shortened Li-H distances occur, which force Li off the static 8c position, producing a "frustrated" Li sublattice with average 25% occupancy on 8c and 24d. We also note that Na$_2$B$_{12}$H$_{12}$ exhibits a short B$_{12}$H$_{12}$$^{2-}$ anion centre to Na$^+$ distance (ca. 4.2 Å), and as such we expect it to undergo a similar first order transition.

While the B$_{12}$H$_{12}$$^{2-}$ reorientational disorder and Li$^+$ ionic conductivity is likely to persist in the H-poor γ-Li$_2$B$_{12}$H$_{12-x}$ polymorph, this feature alone is likely insufficient to explain why the phase has become nanoscopic compared to the strongly crystalline α and β-Li$_2$B$_{12}$H$_{12}$ polymorphs. The creation of the H-poor γ-Li$_2$B$_{12}$H$_{12-x}$ polymorph is clearly related to H loss from Li$_2$B$_{12}$H$_{12}$ and high resolution transmission electron microscopy may elucidate these unique microstructural details. However, light atom evaporation by electron "knock on" damage may preclude the use of Li, even at very low electron flux.[14] We note that Cs$_2$B$_{12}$H$_{12}$ also decomposes to a similar H-poor Cs$_2$B$_{12}$H$_{12-x}$ phase that also diffracts with a broad halo, similar to γ-Li$_2$B$_{12}$H$_{12-x}$. On this basis, decomposed Cs$_2$B$_{12}$H$_{12-x}$ phase would be preferable for high resolution TEM studies to discern the nature of the feature delineating nanoscopic mosaics of Cs$_2$B$_{12}$H$_{12-x}$. The nanoscopic nature of the H-poor γ-Li$_2$B$_{12}$H$_{12-x}$ polymorph is also the major reason why the LiBH$_4$ decomposition process has only recently been clearly elucidated for the first time.[3]

Our findings strongly suggest that the thermodynamics for the decomposition of LiBH$_4$ to the γ-Li$_2$B$_{12}$H$_{12-x}$ polymorph[3] must be reassessed, and that the entropy component of the order-disorder transition in Li$_2$B$_{12}$H$_{12}$ must be included. For example, such entropic features are the origin of the failure to correctly predict the high temperature hexagonal polymorph of LiBH$_4$ by density functional theory.[7] Further *in-situ* studies such as neutron diffraction, quasi-elastic neutron scattering and ^{7}Li spin-lattice relaxation by solid state NMR will yield more details on the complex interplay of B$_{12}$H$_{12}$$^{2-}$ reorientational disorder and Li$^+$ conductivity in the Li$_2$B$_{12}$H$_{12}$ system.

Conclusions

Li$_2$B$_{12}$H$_{12}$ thermally decomposes under vacuum via a previously unobserved discontinuous first-order phase transformation at ca. 355°C. This transformation displays an order-disorder entropic process, consistent with reorientational disordering of the icosahedral B$_{12}$H$_{12}$$^{2-}$ anion, and Li$^+$ conductivity. It also displays the symmetry preserving features of an isosymmetric transformation. During the transition, the unit cell volume expands by ca. 8.7%. Commensurate with H release, the β-Li$_2$B$_{12}$H$_{12}$ polymorph decomposes to a nanoscopic H-poor γ-Li$_2$B$_{12}$H$_{12-x}$ phase. Presently it is not possible to discern the nature of the microstructural feature that delineates the nanoscopic mosaics of γ-Li$_2$B$_{12}$H$_{12-x}$. All thermodynamic modeling related to LiBH$_4$ and Li$_2$B$_{12}$H$_{12}$ decomposition must be modified to include the entropic reorientational disordering of the icosahedral B$_{12}$H$_{12}$$^{2-}$ anion and Li$^+$ conductivity.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Crystallographic structural details of the disordered β-Li$_2$B$_{12}$H$_{12}$ polymorph are provided.]. See DOI: 10.1039/c3cp53090f/

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