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LETTER

Order and disorder in lithium tetrahydroborate

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Introduction

Lithium tetrahydroborate, $LiBH_4$, is an important energy material with a range of significant properties. As a potential hydrogen storage material, it is the lightest of the tetrahydroborates with volumetric and gravimetric hydrogen densities of 121 kg H/m^3 and 18.5 mass%, respectively [1]. At 381 K, $LiBH_4$ undergoes a structural phase transition to a hexagonal superionic phase [2] with a Li^+ ionic conductivity of the order of 10^{-3} S cm^{-1}. Moreover, $LiBH_4$ forms eutectic mixtures with a number of materials, including $LiNH_2$ and CaH_2, which enhance key hydrogen storage properties [3, 4]; $LiBH_4$ also readily absorbs and desorbs ammonia [5] at room temperature and pressure with little structural modification [6]. The crystal structure and, in particular, the endemic disorder in $LiBH_4$ is a key component of these diverse properties. To date, crystallographic analyses have focussed on the average crystal structure which indicates that the transition from the low temperature orthorhombic [7] to the high temperature hexagonal [8] phase is a reconstructive order–disorder transformation. However, little attention has been given to the precise nature of the atomic disorder in $LiBH_4$ which underpins many of its remarkable properties. In this article, it is shown that the disordered nature of the hexagonal phase is apparent even in the low-temperature phase, as long-range order is lost well below the 381 K superionic transition. Indeed, structural correlations beyond 10 Å are not detectable even at room temperature and are only readily observed at low temperatures (50 K).

Experimental

A fully isotopically enriched sample of $^7Li^{11}BD_4$ was synthesised as all the elements of natural abundance in $LiBH_4$ either have high cross-sections for neutron capture (^6Li, ^{10}B), or have considerable incoherent neutron scattering (^1H). A previous study by Hartman et al. [9] reported that the structure of fully isotopically enriched $LiBD_4$ is the same as that of non-enriched $LiBH_4$. $^7Li^{11}BD_4$ was synthesised using a Parr High Pressure Reactor Furnace based on the method of Friedrichs et al. [10]. Crystalline boron-11 (96 + atomic % ^{11}B, 99.9% B, Alfa Aesar) was mechanically milled using a planetary (rotating) ball mill (Retsch PM100) under an argon atmosphere for 30 min at 300 rpm to reduce the particle size. A 125-mL tungsten carbide milling jar with six 20 mm tungsten carbide milling balls were used and the mass ratio of powder to balls was approximately 35:1. The milled boron powder was combined with excess lithium-7 (99%, Sigma-Aldrich) by manually mixing using a pestle and mortar within an argon filled glove box. The material was transferred to the reactor pressure vessel which was then sealed and evacuated before being charged with 55 bar deuterium [CK Gas, D

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99.8%, (D_2 99.6% + HD 0.4%)]. The vessel was heated to 700 °C at a rate of 7 °C/min and remained at 700 °C for 12 h. At the end of the cycle the heating element turned off allowing the vessel to cool to room temperature over a period of approximately 2 h. The resulting dark colored mixture was washed in anhydrous ether under nitrogen using a Schlenk line to separate white $^7Li^{11}BD_4$ from LiD and amorphous boron. The sample was then transferred into a vanadium can within an argon filled glove box and sealed.

Results have been obtained using Pair Distribution Function (PDF) analysis which is based upon the total scattering from a diffraction experiment and thus identifies the local atomic arrangement [11–13]. Variable temperature neutron powder diffraction data were collected on the GEM diffractometer (ISIS Spallation Neutron Source) which is well suited to PDF analysis because of its large Q range. The sample was first cooled to 50 K at 5 K/min and diffraction data were collected. The sample was then warmed at 5 K/min and data were collected at 293, 373, 423, 473, and 523 K. Data were normalised and corrected using GudrunGui2 (based on the ATLAS suite of programs [14]) and subsequent Fourier transforms provided the real space total radial distribution function, $G(r)$ (as defined by Keen [15]), for each dataset.

Results and discussion

Figure 1 shows the $G(r)$ plots for $LiBD_4$ across the temperature range 50–523 K. The most prominent feature in all of the $G(r)$ plots is the B–D bond distance at 1.2 Å, which shows a small increase in length with increasing temperature from 1.200(1) Å at 50 K to 1.210(1) Å at 523 K. The second most prominent peak in the plots is the D···D distance in the $[BD_4]^-$ unit at 1.95 Å, which also increases slightly in length on heating from 1.950(2) Å at 50 K to 1.979(2) Å at 523 K. The ratio of the D···D to B–D distances for 50 and 523 K are 1:1.624(2) and 1:1.635(2), respectively which is in good agreement with the anticipated ratio of 1:1.633 for an ideal tetrahedral geometry [where the expected ratio is $1{:}\left(2\sqrt{2}/\sqrt{3}\right)$]. This, together with the sharpness of the D···D and B–D peaks in all of the $G(r)$ plots, demonstrates that the ideal tetrahedral geometry of the BD_4 anions is not only present in the orthorhombic phase at 50 K, but also maintained in the hexagonal phase at temperatures as high as 523 K. This result has important consequences for future computational studies and is in contrast to the large anisotropic displacement parameters and deviation in bond lengths that have been previously reported for the BD_4 anion in the high temperature phase [7, 9], but supports the observation made by Filinchuk et al. [8] and Buchter et al. [16] that the anions are geometrically very similar in both high and low temperature polymorphs of $LiBH_4$.

The $G(r)$ plot for the 50 K dataset shows distinct peaks even at high r, which is consistent with a long-range order of the local structure [13]. As the temperature increases, the peaks at high r become broad and indistinct as the structure of $LiBD_4$ becomes progressively more disordered. While some increase in the disorder of the structure, and hence broadening of the peaks, can be anticipated because of an

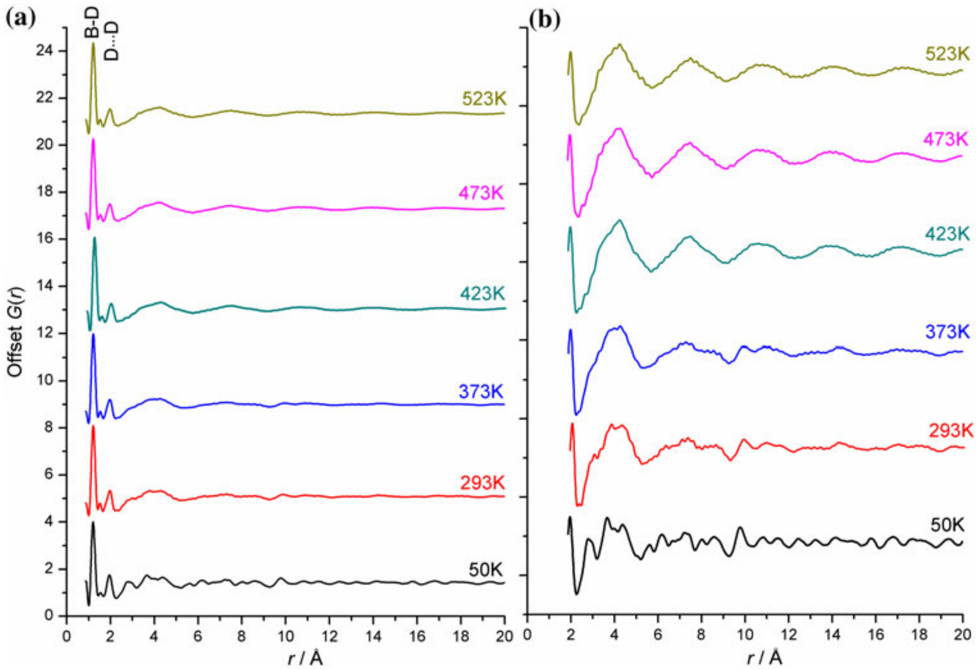

Fig. 1 **a** $G(r)$ plots for $LiBD_4$ over the temperature range of 50–523 K; **b** a magnified view of the higher r features in the $G(r)$ plots for $LiBD_4$ for this temperature range

increase in thermal libration as a function of temperature, the $G(r)$ plots demonstrate that the level of disorder is more significant than this. Notably, the structure shows a significant amount of disorder with ill-defined peaks in the $G(r)$ plot even at room temperature and the 293 K data much more closely resemble the 373 K data than the 50 K data. Hartman et al. [9] have alluded to the possibility of large amplitude librational and re-orientational motions "well below the structural transition" to the high temperature hexagonal phase based on neutron powder diffraction data collected at 360 K.

Given the small scattering cross-section of ^{7}Li compared with both ^{11}B and D, it is not possible to infer much about the Li disorder in $LiBD_4$. Electrical conductivity measurements by Matsuo et al. [2] show that the low temperature phase has a poor ionic conductivity, most likely resulting from the geometrical arrangement of the ordered orthorhombic structure which inhibit the formation of facile ion channels. However, Matsuo et al. also report an increase in electrical conductivity below the phase transition (between 330 and 390 K) of one order of magnitude. Our results indicate that significant orientational disorder of the $[BD_4]^-$ unit begins to occur at a substantially lower temperature than is observed for the premonitory increase in ionic conductivity which is associated with Li^+ motion. It is thus likely that the intrinsic orientational disorder of the BD_4 anions promotes the formation of facile ion channels that allows the Li^+ ions to move which, in turn, may well be one of the principal causes of the orthorhombic–hexagonal transition itself. While the PDF analysis is unable to determine the detailed nature of Li^+ disorder, it is worth noting that in $La_{2/3-x}Li_{3x}TiO_3$, a compound subject to wide investigation as a solid lithium electrolyte due to its high lithium capacity, Yashima et al. [17] also observe Li^+ ionic disorder at room temperature.

While most features above 2.4 Å in the 293 and 373 K plots are broadened, a significant trough at approximately 9.2 Å followed by a positive peak at approximately 9.8 Å can be readily identified. These features can be seen in each of the 50, 293, and 373 K plots, and they are observed to decrease in amplitude with increasing temperature, thus further indicating the increase in disorder with heating. Another peak which behaves similarly is seen at 2.8 Å in the 50 K plot, and is mainly contributed to by D···D interactions between adjacent $[BD_4]^-$ units (Fig. 2). The disappearance of this peak and the decrease in the peak at 9.8 Å on heating indicates that the BD_4 anions are significantly orientationally disordered, which is achieved through rotation of the BD_4 anion. The peak associated with the interionic D···D distances becomes considerable broader with increasing temperature while that associated with the central B atom (which is essentially stationary) and contributed to by B···B interactions at 9.8 Å is retained, even at 373 K. This is in contrast to ab initio potential energy landscape calculations made by Buchter et al. [16], which indicate that in the low temperature phase the BH_4 anions are ordered with fairly localized minima and barriers higher than 0.6 eV. However, Hartmann et al. [9] observe increased atomic displacements for $LiBH_4$ at 360 K compared to those observed at 3.5 K, which the authors attribute to libration and dynamical disorder.

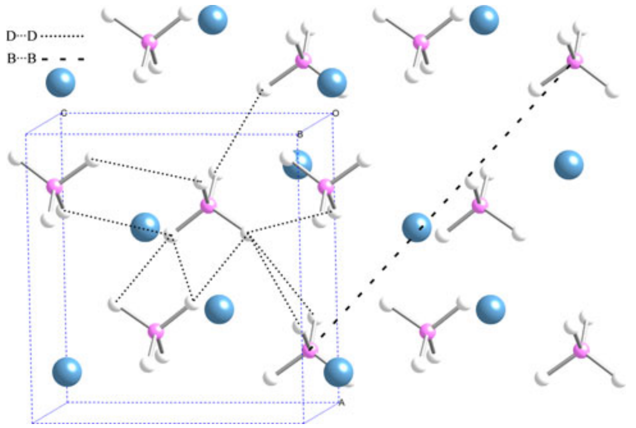

Fig. 2 D···D and B···B distances of ~2.8 and ~9.8 Å, respectively in the $LiBD_4$ low temperature phase

The phase transition from the low temperature phase to the high temperature phase (at 381 K) [18] can be identified from the different characteristics apparent in the $G(r)$ plots at 50, 293, and 373 K compared with those at 423, 473, and 523 K. The degree of disorder in the high temperature $P6_3mc$ phase has been a point of issue for both theorists and experimentalists. Indeed Filinchuk et al. [8] note that "even precise structural data alone cannot give an answer to the question of whether the large observed libration parameters for the hexagonal phase are due to a softening of the libration phonons or result from a low-energy dynamic and/or static disorder of the BH_4 group". The $G(r)$ plots demonstrate a level of rotational disorder that is larger than can be expected solely from atomic libration as no discernible features are visible for r greater than 2.3 Å. Moreover, these data also show that the ideal tetrahedral geometry of the BD_4 anions is not only seen in the orthorhombic phase at 50 K, but is also maintained in the hexagonal phase at high temperatures. This confirms that the ideal tetrahedral BD_4 anions are highly orientationally disordered in the high temperature phase thus resulting in a pair distribution function that is more reminiscent of a liquid than a solid. These results therefore define the local nature of the structure and BD_4 disorder in lithium tetrahydroborate which are key to its diverse properties in both the low and high temperature phases.

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