Experimental report

29/08/2022

Proposal: **5-24-686** **Council:** 4/2021

Title: The effect of high temperature on the structure of solid solution Na(BH4)(1-x)Ix

Research area: Chemistry

This proposal is a new proposal

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Samples: Na(BH4)0.7I0.3
Na(BH4)0.9I0.1
Na(BH4)0.1I0.9
Na(BH4)0.3I0.7
Na(BH4)0.5I0.5

Instrument	Requested days	Allocated days	From	To
D1B	4	2	04/10/2021	06/10/2021

Abstract:

Solid solutions of sodium borohydride and sodium iodide have been studied for their potential as sodium-ion battery electrolytes, but have displayed discontinuous behaviour when measuring temperature-dependent EIS, which varies with composition. This leads to interest in how the composition may affect the structure and/or structural changes at elevated temperatures. 5 samples will be studied, from room temperature up to 350C, with iodide content increasing by 20% with each sample. The samples will be enriched with isotopes 11B and 2H to improve their neutron performance, and allow study of these lightweight structures which is impossible with X-ray diffraction.

PROPOSAL 5-24-686

THE EFFECT OF HIGH TEMPERATURE ON THE STRUCTURE OF SOLID SOLUTION NA$(BH_4)_{1-x}I_x$

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Introduction

Previous work showed that $Li(BH_4)_{1-x}Br_x$ was an excellent lithium ion conductor, with BH_4^- tumbling being crucial to the mechanism of ionic conduction. sodium borohydride has a cubic structure across a very wide range of temperatures and pressures. This is the same structure as the sodium halides, and so it is possible that a solid solution may be formed without great difficulty. A solid solution of the form $Na(BH_4)_{1-x}I_x$ was produced, but it was not known whether this structure was stable to high temperature, or if it would undergo a change. In addition to this, the borohydride unit cannot be studied using X-ray diffraction due to the extreme lightness of these elements. Therefore, the RT and HT powder neutron diffraction patterns of an assortment of materials from this solid solution were sought.

Experimental Setup

Samples of powder were loaded into vanadium cans with a small amount of indium wire used to ensure a tight seal. These were sealed inside a glovebox in Glasgow before being sent on to ILL. In-situ PND measurements were carried out on D1B at ILL in Grenoble by Ines Puerte Orenche at RT for x=0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, & 0.9, and data was collected at 673 K for x=0.1, 0.5, 0.7 & 0.9. Shorter measurements were also taken at intermediate temperatures for these samples.

Results

Rietveld refinement of the room temperature data was used to determine the iodide content with a high degree of accuracy, and to relate this to the changes in the unit cell (table 1, figure 1). The occupancy of the B/I site was constrained to a sum of 1, i.e. the possibility of vacancies was not allowed.

Table 1 Unit cell parameters for values all values of x alongside their refined iodide occupancies and the statistics of the refinement

x	a (Å)	V (Å^3)	*Iodide occupancy*	R_p	R_{wp}	χ^2
0.1	6.1822 (2)	236.28 (2)	0.088 (10)	2.07	2.65	1.21
0.2	6.2244 (2)	241.15 (2)	0.182 (8)	1.92	2.39	1.03
0.3	5.2534 (4)	244.56 (3)	0.284 (10)	3.26	4.13	2.95
0.4	6.2870 (3)	248.50 (2)	0.381 (7)	1.98	2.49	1.40
0.5	6.3239 (3)	252.90 (2)	0.483 (7)	1.89	2.40	1.09
0.6	6.3472 (2)	255.71 (2)	0.580 (5)	1.82	2.32	1.11
0.7	6.3921 (2)	261.17 (1)	0.712 (4)	1.55	1.93	1.12
0.8	6.4133 (2)	263.79 (1)	0.802 (3)	1.73	2.22	1.19
0.9	6.4432 (1)	267.48 (1)	0.897 (2)	1.44	1.86	1.05

It was found that the unit cell increased linearly as the iodide content increased. Since both the parent compounds are simple cubic structures, this is as expected. Additionally, it was possible to refine the position of the deuterium atom, and so obtain accurate bond lengths for the BD_4^- unit. The change in the positions, which is as a fraction of the unit cell, is given in figure 3, and the concomitant change in the B-D bond lengths are given in figure 4.

It was found that the position of the deuterium atom trended towards the centre of the cell, where the B/I site is as defined by symmetry constraints, as the value of x increased. Beyond x=0.5, it began to trend away again, until the highest values of x. Additionally, the B-D bond length became shorter towards x=0.5, and subsequently lengthened. This suggests that the borodeuteride unit in the sample with 50% iodide content is the most compact. In both instances, the values for x=0.9 diverge a little from what might be expected; this is likely because of the very low borodeuteride content in this sample, which makes getting accurate values for D more difficult.

The thermal parameters were also investigated. Due to symmetry constraints, B and I could not be deconvoluted from one another, and both this site and the Na site were limited to isotropic refinement. How these values change is shown in Fig 4. The thermal parameter for x=0.3 could not be refined; as shown in Fig 1, this sample had larger statistical errors than the other values, although the data was not observably worse.

The sample with x=0.5 had the largest thermal parameter for both Na and B/I, indicating that this sample had the greatest degree of thermal motion. Generally, as x increased towards 0.5, B_{iso} of Na increased, and above 0.5, it decreased again. This is likely because, as the degree of substitution increases, there is more irregularity in the structure, which allows greater movement of the individual ions. Towards either extreme, the samples are more homogenous, and so there is less disorder. It is possible that this indicates that there are more vacancies in samples with intermediate values of x. This aligns with what was shown in the EIS data – that the movement of the sodium ion is easiest for x=0.5, and easier for values of x closer to this value. A simulation of the structure is given in figure 5, showing the thermal displacement of the deuterium atoms. The large flat oval shape is quite suggestive of the tumbling movement of the unit; it is clear that the deuterium atoms do not move significantly away from the central boron, and most of the movement is directed laterally.

Powder patterns were collected at 400 °C for 4 samples: x=0.1, 0.5, 0.7 & 0.9. Rietveld refinement was performed on the high-temperature data in the same way as was done with the room-temperature data; the results of this are given in table 2.

Table 2 Unit cell parameters for $Na(BD_4)_{1-x}I_x$ for selected values of x at 298 K and 623 K

x	*a (Å) 298 K*	*a (Å) 623 K*	**Absolute increase**	**% increase**	*V (Å³) 298 K*	*V (Å³) 623 K*	**% increase**	**Absolute increase**
0.1	6.1822	6.3405	*0.1583*	*2.56*	236.28	254.9	*7.88*	*18.62*
0.5	6.3239	6.4678	*0.1439*	*2.28*	252.9	270.56	*6.98*	*17.66*
0.7	6.3921	6.521	*0.1289*	*2.02*	261.17	277.3	*6.17*	*16.12*
0.9	6.4432	6.5651	*0.1219*	*1.89*	267.49	282.96	*5.78*	*15.47*

While no change in symmetry was observed on heating, it was found that the unit cell of the samples with greater borodeuteride content increased by a larger amount than the samples with more iodide, even though, at room temperature, increasing iodide content results in a linear increase in unit cell size, as shown in table 2. This is surprising, because the iodide ion is larger than the borohydride ion (220 pm[12] vs 205 pm[13]), and the substitution of hydride for deuteride results in a small contraction. Indeed, the unit cell of the material with only 10% iodide content had not only a greater percentage increase, but also absolute change, as shown in table X, over the sample with 90% iodide. This is indicative of the much greater dynamic movement of the borohydride ion, which has been shown in prior studies to demonstrate a tumbling motion.[8] The iodide ion is more wholly symmetrical, and so the motion of the borohydride ion is more dramatic. Since ionic motion increases with increasing temperature, it is therefore not surprising that with increasing borohydride content we get a greater volume expansion. It is possible that this greater expansion is beneficial to the ionic conductivity of samples with intermediate values of x, but that the intense thermal movement of the borodeuteride ion when it is in higher concentration is inhibitive to the movement of the sodium ion.

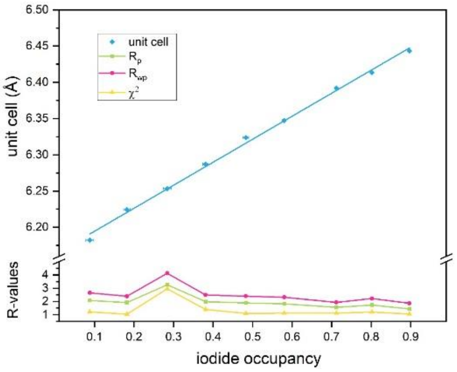

Figure 2 Refined iodide occupancies & unit cell parameters of $Na(BH_4)_{1-x}I_x$

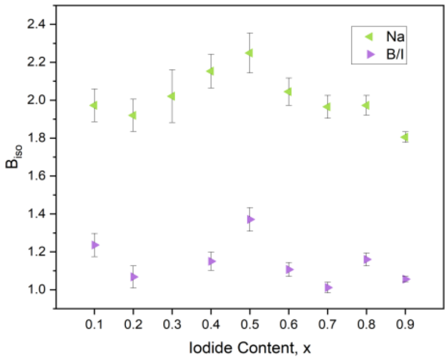

Figure 2 Change in isotropic thermal parameters for Na and B/I positions with iodide content

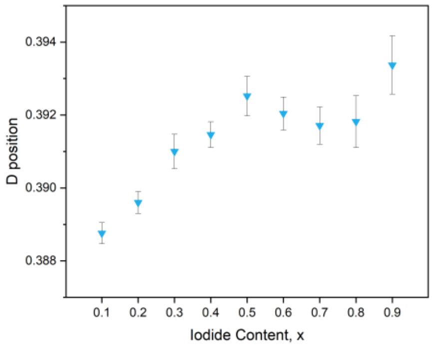

Figure 3 Change in the absolute position of the Deuterium atom in $Na(BD_4)_{1-x}I_x$ with changing x

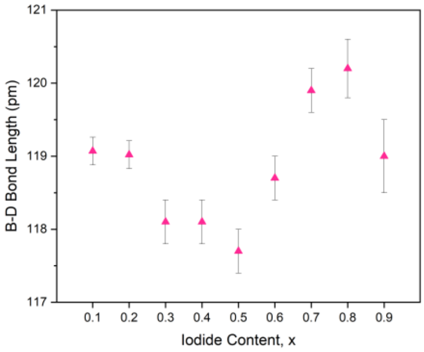

Figure 4 Change in B-D bond length in $Na(BD_4)_{1-x}I_x$ with changing x

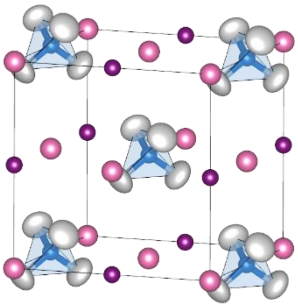

Figure 5 Structure of $Na(BD_4)_{0.5}I_{0.5}$. BD_4 and I positions are randomised; for better illustration of the BD_4^- unit. Blue spheres are boron, Pink spheres are sodium, Purple spheres are iodine, Grey spheres are deuterium