

Sodium superionic conduction in  $\text{Na}_2\text{B}_{12}\text{H}_{12}^\dagger$ 

Cite this: *Chem. Commun.*, 2014, 50, 3750

Received 27th December 2013,  
Accepted 20th February 2014

DOI: 10.1039/c3cc49805k

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Impedance measurements indicate that  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  exhibits dramatic  $\text{Na}^+$  conductivity (on the order of  $0.1 \text{ S cm}^{-1}$ ) above its order-disorder phase-transition at  $\approx 529 \text{ K}$ , rivaling that of current, solid-state, ceramic-based, Na-battery electrolytes. Superionicity may be aided by the large size, quasispherical shape, and high rotational mobility of the  $\text{B}_{12}\text{H}_{12}^{2-}$  anions.

Lithium-ion-based batteries have come to dominate the global portable-energy arena. However, Li is a relatively high-cost element. Moreover, the likelihood of future cost increases, due to dwindling supplies and burgeoning demand exacerbated by the emergence of electric vehicles, has heightened the need to find cheaper alternative technologies. The next heavier alkali metal element, Na, is much more abundant and much less expensive than Li, making batteries based on Na ion conduction worthy candidates for further consideration, especially for larger-scale, stationary energy-storage applications. Recent reviews of Na-ion battery technology have been given by Ellis and Nazar<sup>1</sup> and Hueso *et al.*<sup>2</sup> Sodium batteries based on Na-S and Na-NiCl<sub>2</sub> technologies<sup>3,4</sup> have been commercially available for many years, typically employing a solid-state Na  $\beta''$ -alumina electrolyte. Further improvements in the electrolyte material may ultimately lead to increased commercial use for these types of batteries, even for vehicular applications, resulting in significant cost savings. Here we report on the discovery of an exceptional new solid-state Na superionic conductor,

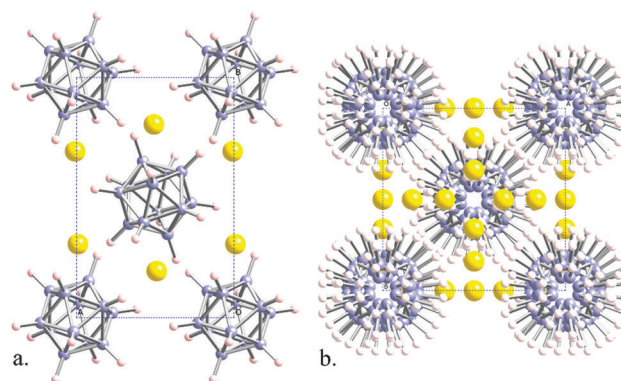


Fig. 1 Unit cells of the (a) low-temperature ordered monoclinic and (b) high-temperature disordered cubic  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  structures viewed along the  $c$ -axes. Yellow, purple, and white spheres represent Na, B, and H, respectively.

$\text{Na}_2\text{B}_{12}\text{H}_{12}$ , a complex hydride comprised of  $\text{Na}^+$  cations and large dodecahydro-*closo*-dodecaborate ( $\text{B}_{12}\text{H}_{12}^{2-}$ ) polyanions. The fast conduction is enabled by an order-disorder structural phase transition.

Fig. 1 depicts the  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  low-temperature ordered monoclinic<sup>5</sup> and high-temperature disordered, body-centered-cubic (bcc) phases.<sup>6</sup> Upon first-order transformation with heating to the latter phase near 529 K, the quasispherical, icosahedral  $\text{B}_{12}\text{H}_{12}^{2-}$  anions undergo bcc packing with significant orientational disorder, represented schematically by a variety of superimposed anion orientations in Fig. 1b. In contrast to the fully-occupied cation sites of the low-temperature ordered structure, the  $\text{Na}^+$  cations in the high-temperature structure are disordered among a complex sublattice of off-center sites within the relatively large distorted tetrahedral interstices of the anions. The disordered structure is akin to the superionic conducting  $\alpha$ -phase of AgI,<sup>7</sup> except that the preferred  $\text{Ag}^+$  cation sites are believed to be in the center of the relatively smaller tetrahedral interstices of the bcc  $\Gamma^-$  sublattice. The similarities between the two systems suggested that a mobile “melted”  $\text{Na}^+$  cation sublattice capable of superionic conduction may be present in the disordered bcc  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  phase. Indeed, recent  $^{23}\text{Na}$  NMR measurements of  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  by Skripov *et al.*<sup>8</sup>

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<sup>†</sup> Electronic supplementary information (ESI) available:  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  synthesis/stability and experimental details. See DOI: 10.1039/c3cc49805k

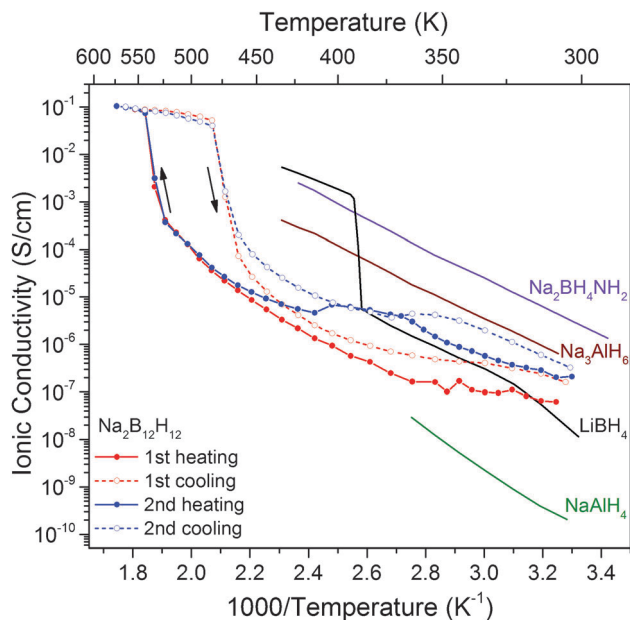


Fig. 2 Temperature dependence of the ionic conductivity of  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  compared with that for other complex hydride materials:  $\text{NaAlH}_4$ ,<sup>9</sup>  $\text{Na}_3\text{AlH}_6$ ,<sup>9</sup>  $\text{Na}_2\text{BH}_4\text{NH}_2$ ,<sup>10</sup> and  $\text{LiBH}_4$ .<sup>11</sup> Standard uncertainties are commensurate with the observed scatter in the data.

indicated an enhancement in the  $\text{Na}^+$  cation jump rate to more than  $2 \times 10^8$  jumps  $\text{s}^{-1}$  upon transformation to the high-temperature phase.

Based on the nature of the disordered  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  structure and the  $^{23}\text{Na}$  NMR results, we decided to explore the Na ion conductivity as a function of temperature across the phase transition. The conductivity of an unsintered pressed  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  pellet was determined by the AC complex impedance method using a pair of Au foils as electrodes.

Fig. 2 plots the conductivity upon heating and cooling across the transition, in comparison with other complex hydride materials. It is clear that  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  undergoes a dramatic, nearly thousand-fold enhancement in conductivity upon transformation to the cubic phase, with values approaching and exceeding  $0.1 \text{ S cm}^{-1}$  between 540 K and 573 K. While not measured, further conductivity increases are expected with increasing temperature until the onset of  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  decomposition above  $\approx 860 \text{ K}$ .<sup>6</sup> Hysteretic behavior is evident upon cooling, with superionic conductivity lingering until  $\approx 480 \text{ K}$ , at which point there is a precipitous drop concomitant with the known reversion back to the low-temperature monoclinic structure.<sup>6</sup> Although the high-temperature conductivity is reproducible upon subsequent cycling, the apparent conductivity associated with the monoclinic structure is less so. This reflects the fact that the back-transformation upon cooling is known to be sluggish, and, depending on the cycling details, a small fraction of the cubic phase can persist with the monoclinic phase for finite periods of time below the expected phase transition temperature. Hence, the exact conductivity is, at least in part, a reflection of the percolation of Na ions through the slowly evolving mixed-phase material.

The complex impedance plots at various temperatures in Fig. 3 consist of an arc in the high-frequency range and a spike

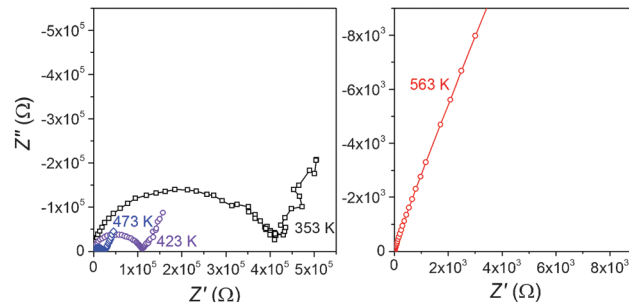


Fig. 3 Complex impedance plots of  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  measured at various temperatures during heating run.

in the low-frequency range corresponding to contributions from the bulk/grain boundaries and the electrode, respectively, while no arc is observed at 563 K. The results suggest that  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  behaves as a typical ionic conductor. We note that it is difficult to separate the bulk and grain boundary contributions because two overlapping high- and low-frequency arcs are not clearly seen in Fig. 3.

The dramatic rise in conductivity across the phase transition for  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  mimics  $\text{AgI}$  behavior<sup>12</sup> and indicates the profound advantage that disordered, cation-vacancy-rich structures such as cubic  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  and  $\text{AgI}$  have over their lower-temperature ordered structures to facilitate fast conduction. This effect can also be seen in the conductivity behavior for  $\text{LiBH}_4$  in Fig. 2, where the jump in Li ion conductivity signals a phase change to a hexagonal structure with  $\text{Li}^+$  cation disorder.<sup>13,14</sup>

Visual extrapolation of the conductivity associated with cation-ordered  $\text{NaAlH}_4$  and  $\text{Na}_3\text{AlH}_6$  complex hydrides in Fig. 2 to 480 K and above suggests much lower conductivity values than for cubic  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  at the same temperatures. In contrast, extrapolated conductivity values for  $\text{Na}_2\text{BH}_4\text{NH}_2$  compare more favorably to those of cubic  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ . This high conductivity behavior reflects the disordered nature of the antiperovskite  $\text{Na}_2\text{BH}_4\text{NH}_2$  structure<sup>15</sup> in this temperature regime, with one-third of the cation sites vacant and accessible for diffusion, reminiscent of cubic  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ . Yet, unlike  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ ,  $\text{Na}_2\text{BH}_4\text{NH}_2$  melts at 492 K.<sup>15</sup>

Besides the presence of cation vacancies, the anion/cation size ratio is also a potentially key factor affecting conductivity since larger anions lead to enlarged interstitial diffusion pathways. However, a direct comparison between different complex hydrides in Fig. 2 is clouded by several factors, including the differences in structures, anion valence numbers, and anion/cation stoichiometric ratios, as well as the presence of mixed phases (in the case of  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ ). Nonetheless, it is probable that the overly large, quasospherical  $\text{B}_{12}\text{H}_{12}^{2-}$  anion provides for more facile cation pathways with lower activation energy barriers for diffusion, as reflected by the relatively shallow slope of the cubic  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  conductivity with temperature compared to the other materials with smaller anions in Fig. 2. The derived activation energy of 0.21(1) eV is indeed lower than the values of 0.79 eV and 0.62 eV reported for  $\text{NaAlH}_4$  and  $\text{Na}_3\text{AlH}_6$ , respectively,<sup>9</sup> and 0.61(1) eV derived from the  $\text{Na}_2\text{BH}_4\text{NH}_2$  conductivity data.<sup>10</sup> It would be highly advantageous to be able to stabilize the disordered cubic  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  phase at lower temperatures, since, from visual extrapolation, we expect that fast ion conduction

would be maintained down to room temperature due to the low diffusion barrier associated with this structure.

Finally, it still is not clear what effect the degree of reorientational mobility of the polyanion has on cation conductivity. This refers to the so-called paddlewheel mechanism<sup>16</sup> for diffusion where the rotating anions surrounding the cations may possibly aid cation diffusional jumps. While there should be little or no effect for complex hydrides with more orientationally immobile anions, the presence of rapid anion reorientations in these types of materials may augment conductivity. For Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub>, <sup>1</sup>H and <sup>11</sup>B NMR measurements<sup>8</sup> indicate a nearly hundred-fold increase in the anion reorientational jump rate (to the order of 10<sup>11</sup> jumps s<sup>-1</sup>) upon transformation to the cubic phase. This is orders of magnitude higher than the observed Na<sup>+</sup> diffusional jump rate,<sup>8</sup> suggesting that the rapidly spinning B<sub>12</sub>H<sub>12</sub><sup>2-</sup> anions may indeed be acting as a “lubricant” for Na<sup>+</sup> diffusion. Further systematic studies are necessary to ascertain the importance of anion mobility in facilitating cation diffusion.

Anion and cation disorder is the entropic driving force for the order-disorder transition in this material. The phase transition temperature depends to large extent on the enthalpic change accompanying the transition to the dynamically disordered state. Thus, one can possibly lower the transition temperature by attempting to alter the relative enthalpies of the ordered and disordered states by varying the anion/cation size ratio or the polyanion symmetry. For example, this can be accomplished through chemical modifications such as partial or full anion halogenation or partial substitution of B<sub>12</sub>H<sub>12</sub><sup>2-</sup> with other anions such as halides. This may have the secondary effect of also enhancing the Na<sup>+</sup> conductivity and/or changing the disordered structure to a different (possibly preferable) form altogether. These considerations suggest further investigations with other related fast-ion-conductor systems based on Li<sup>+</sup>, K<sup>+</sup>, or Mg<sup>2+</sup> cations. For example, the recently reported disordered face-centered-cubic phase of Li<sub>2</sub>B<sub>12</sub>H<sub>12</sub> (ref. 6, 17 and 18) forms upon heating by ≈615 K, but this probable fast-ion conductor is unstable at this temperature and slowly decomposes with time. Appropriate chemical modifications as mentioned above could help lower the transition temperature in this system and further stabilize the disordered phase.

It should be noted that, even though Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub> has a somewhat high transition temperature, the two commercial solid-state Na battery systems are designed to operate above this temperature near 573 K.<sup>1,2</sup> Since the conductivity of cubic Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub> rivals that of Na β"-alumina<sup>19,20</sup> in this temperature region, it would be worth investigating the feasibility of Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub> as an alternative electrolyte in such systems. Decreasing the transition temperature with modified materials would enable additional uses in next-generation Na batteries requiring lower operating temperatures.<sup>2,21</sup>

In conclusion, we have shown that disordered cubic Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub> displays dramatically high superionic conductivity, approaching and exceeding 0.1 S cm<sup>-1</sup> between 540 K and 573 K. Upon cooling, this superionic phase lingers until ≈480 K, due to structural hysteresis. The favorable conductivity, relative insensitivity to air,

high-temperature stability, simplicity of preparation, and low cost all make Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub> and related Na-containing polyanion materials an intriguing class of compounds for further studies as next-generation Na superionic electrolytes. Moreover, analogous polyanion systems incorporating Li<sup>+</sup>, K<sup>+</sup>, or Mg<sup>2+</sup> cations are potentially fruitful additional systems to explore for favorable fast-ion conduction properties and also merit thorough investigations.

This work was performed, in part, in collaboration between members of IEA HIA Task 32–Hydrogen-based Energy Storage. The authors gratefully acknowledge support from DOE EERE through Grant No. DE-EE0002978 and DE-AC04-94AL85000; the Russian Foundation for Basic Research under Grant No. 12-03-00078; the U.S. Civilian Research & Development Foundation (CRDF Global) under Award No. RUP1-7076-EK-12; the National Science Foundation under Cooperative Agreement No. OISE-9531011; the Integrated Materials Research Center for the Low-Carbon Society (LC-IMR), Tohoku University; the Advanced Low Carbon Technology Research and Development Program (ALCA) from the Japan Science and Technology Agency (JST); and JSPS KAKENHI under Grant No. 25220911. The authors also thank Andrew J. Udovic for valuable discussions concerning this work.

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## Supporting information for:

### “Sodium Superionic Conduction in Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub>”

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### Synthesis of Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub>:

The compound was prepared from Cs<sub>2</sub>B<sub>12</sub>H<sub>12</sub> via an ion-exchange method, as in: Her *et al.*, *J. Phys. Chem. C*, 2009, **113**, 11187. In a typical synthesis, around 2 g Cs<sub>2</sub>B<sub>12</sub>H<sub>12</sub> was dissolved upon heating in 80 mL H<sub>2</sub>O and the warm solution was passed through an Amberlite<sup>1</sup> IR-120 ion-exchange column in H<sup>+</sup> form. The acidic fraction, aqueous (H<sub>3</sub>O)<sub>2</sub>B<sub>12</sub>H<sub>12</sub>, was collected and neutralized with 0.1 M aqueous NaOH at room temperature until reaching a pH of 7. The solvent was removed using a rotary evaporator at 323 K and the resulting solid was dried for around 4 h in vacuum at 623 K. The room-temperature, monoclinic, anhydrous Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub> structure was verified by x-ray powder diffraction.

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<sup>1</sup> The mention of all commercial suppliers in this paper is for clarity. This does not imply the recommendation or endorsement of these suppliers by NIST.

### **Experimental Procedures:**

The ionic conductivities were determined in heating and cooling runs repeatedly in the temperature range between 303 K and 573 K by the AC complex impedance method using an NF FRA5097 frequency response analyzer over a frequency range of 10 Hz to 10 MHz. All measurements were performed under Ar. The powder sample was pressing into a pellet  $\approx 8$  mm in diameter and  $\approx 3$  mm in thickness without sintering. This corresponded to a pellet density of  $\approx 1.13$  g/cc, which is close to the bulk density of  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ . Au foils were used as electrodes and were mechanically fixed on both faces of the pelletized sample. The resistances of the sample were obtained by least square fittings of a single arc in the high-frequency range using equivalent circuits of a parallel combination of a resistance and a capacitance. At high temperature, since only a spike caused by the electrode contribution was observed, the resistance values were calculated from the intercept of the spike.



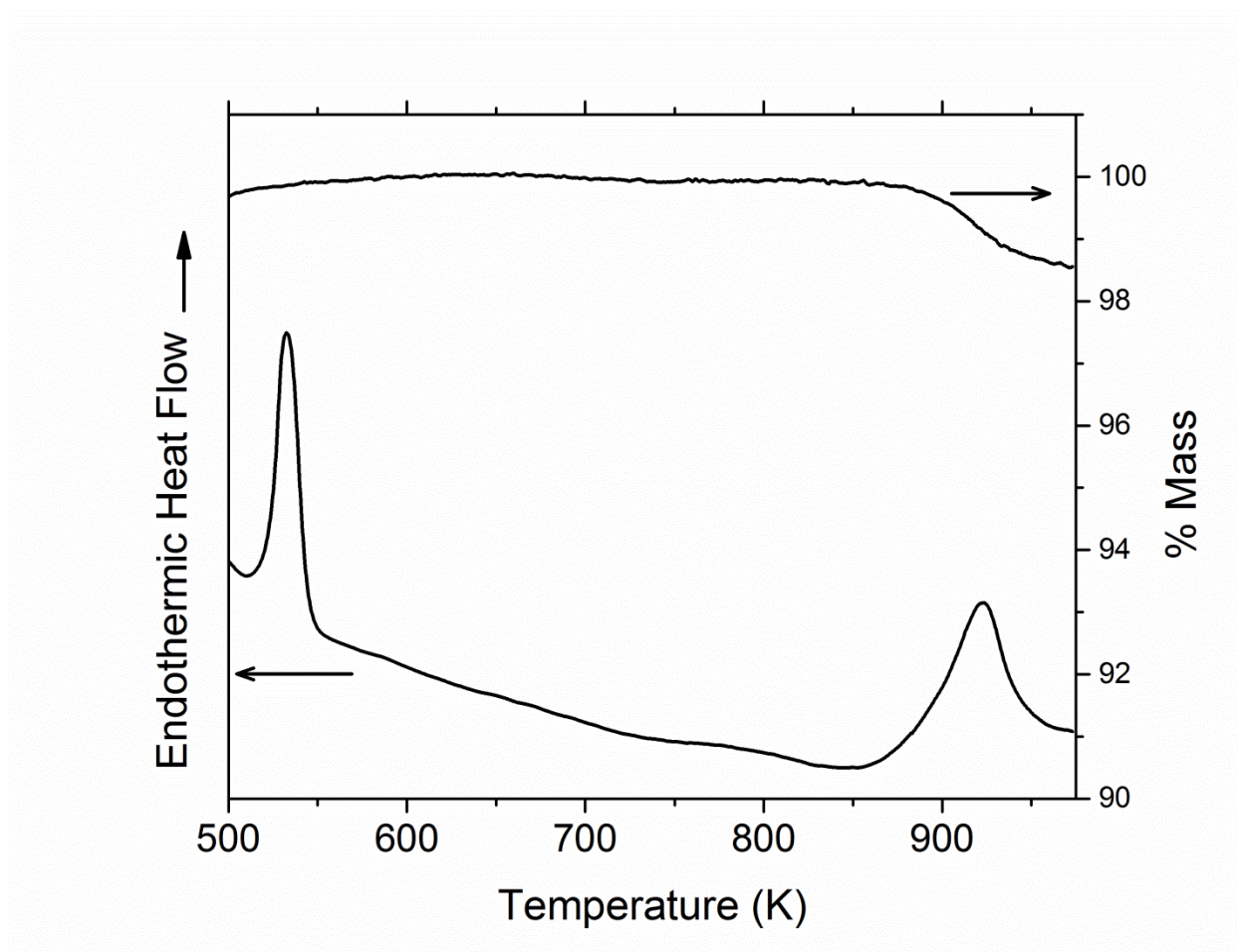


Figure S1. The DSC (left axis) and TGA (right axis) measurement of  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  show the phase transition at 529 K (upon heating from room temperature, 5 K/min). The endothermic peak above 860 K signals decomposition and is accompanied by a 1.1 % mass loss.  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  is stable below this temperature.