ELSEVIER

Contents lists available at ScienceDirect

Energy Storage Materials

journal homepage: www.elsevier.com/locate/ensm



Stabilizing lithium and sodium fast-ion conduction in solid polyhedral-borate salts at device-relevant temperatures



Wan Si Tang^{a,b}, Motoaki Matsuo^c, Hui Wu^a, Vitalie Stavila^d, Atsushi Unemoto^e, Shin-ichi Orimo^{c,e,*}, Terrence J. Udovic^{a,*}

^a NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-6102, United States

^b Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2115, United States

^c Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

^d Energy Nanomaterials, Sandia National Laboratories, Livermore, CA 94551, United States

^e WPI-Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

ARTICLE INFO

Article history: Received 3 February 2016 Received in revised form 17 March 2016 Accepted 18 March 2016 Available online 31 March 2016

Keywords: Ball-milling Closo-borate Nanostructure Phase transition Superionic conductor

1. Introduction

Most of today's rechargeable batteries operate with liquid organic electrolytes, which not only present challenges concerning such matters as capacity fade and overall cycle life, but also make these batteries inherently prone to possible leakage, flammability, and Li-dendrite penetration and shorting. There has been a push to develop alternative solid-electrolyte technologies to address these concerns. One broad class of materials that has recently gained notice involves ionic compounds with complex hydride anions [1]. These compounds typically undergo order-disordertype phase transitions to fast-ion-conducting structures with orientationally mobile anions, LiBH₄ being one prototypical example [2]. These structures are aided by the configurational entropy increase that accompanies the orientational disordering of the polyatomic anions and site disordering of the cations.

More recently, we have shown that an increase in complexhydride-anion size has a markedly positive effect on the fast-ion conductivity of the disordered phase. Indeed, the *closo*-borate compounds $Na_2B_{12}H_{12}$ [3], $Na_2B_{10}H_{10}$ [4] $NaCB_{11}H_{12}$ [5], $LiCB_{11}H_{12}$

ABSTRACT

By a variety of techniques including X-ray powder diffraction, quasielastic neutron scattering, and AC impedance, we have probed the effect of mechanical milling on the phase behaviors of the different lithium and sodium *closo*-borate salt compounds containing $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$, and $CB_{11}H_{12}^{-}$ anions. We have found that the crystallite-size reduction and disordering effects of such milling enables the room-*T* stabilization of their high-*T*-like superionic-conducting phases. This demonstrates a viable strategy for better exploiting the impressive cation mobilities that are typically restricted to somewhat higher temperatures for this class of compounds.

© 2016 Elsevier B.V. All rights reserved.

[5], NaCB₉H₁₀ [6], and LiCB₉H₁₀ [6] with their overly large, cagelike anions exhibit exceptional ionic conductivities of ~0.1 S cm⁻¹ (540 K), 0.01 S cm⁻¹ (383 K), 0.12 S cm⁻¹ (383 K), 0.15 S cm⁻¹ (403 K), 0.05 S cm⁻¹ (323 K), and 0.04 S cm⁻¹ (357 K), respectively, just above their phase transition temperatures T_{trans} . The high cation mobilities are presumably aided by the spacious (and partially vacant) interstitial pathways afforded by the packing arrangement of the orientationally mobile, $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$, $CB_{11}H_{12}^{-}$, and $CB_9H_{10}^{-}$ anions [3–10]. Similar exceptional ionic conductivities are expected for the Li₂B₁₂H₁₂ and Li₂B₁₀H₁₀ analogs, but only well in excess of 600 K [7,9,11,12].

Despite the high ionic conductivities of the binary *closo*-borate compounds, their widespread commercial use as solid electrolytes requires a strategy to stabilize their superionic disordered structures at lower device-relevant temperatures, i.e., at 295 K and below. Besides a possible reduction in $T_{\rm trans}$ via appropriate chemical modifications, we found [5] that low-*T* stabilization of these superionic structures could be realized by morphological modification, via ball-milling, which is known to reduce the crystallite size in solids as well as introduce nano-defects such as vacancies, interstitial sites, dislocations, grain boundaries and stacking faults. This is in line with a recent Li₂B₁₂H₁₂ study, which reported fastion conductivity at room temperature after only briefly milling the material, albeit at high energy [13]. This stabilization is not uncommon. Ball-milling of rutile MgH₂, e.g., leads to the low-*T*

^{*} Corresponding authors. *E-mail addresses*: orimo@imr.tohoku.ac.jp (S.-i. Orimo), udovic@nist.gov (T.J. Udovic).

stabilization of high-*T* orthorhombic γ -phase [14]. Corundum α -phase Al₂O₃ adopts the higher-entropy γ -phase polymorph when the crystallites are nanosized [15]. Finally, Li₃N is known to adopt its higher-pressure β -phase polymorph when confined inside carbon nanopores [16].

Here we report the room-*T* stabilization, by ball-milling, of high-*T*-like disordered phases for all lithium and sodium *closo*borate compounds studied, namely: $Li_2B_{12}H_{12}$, $Li_2B_{10}H_{10}$, $LiCB_{11}H_{12}$, $Na_2B_{12}H_{12}$, $Na_2B_{10}H_{10}$, and $NaCB_{11}H_{12}$. Select AC impedance measurements for ball-milled $Na_2B_{12}H_{12}$ and $Li_2B_{12}H_{12}$ confirmed dramatic increases in room-*T* ionic conductivities compared to the pristine materials. In addition, we found that ball-milling mixtures of these materials can lead to mixed-polyhedral-anion compounds as well as room-*T* stabilization of their own disordered phases. The success of such morphological modification with the additional potential to tailor the anion (and cation) composition opens up exciting new avenues for exploiting the impressive superionic properties associated with these large-anion materials.

2. Experimental details

Li₂B₁₂H₁₂, LiCB₁₁H₁₂, Na₂B₁₂H₁₂, Na₂B₁₀H₁₀, and NaCB₁₁H₁₂ were obtained from Katchem. Li₂B₁₀H₁₀ was synthesized as reported in Ref. [12]. ¹¹B-enriched Na₂¹¹B₁₂H₁₂ (preferred for neutron scattering experiments) was prepared according to Ref. [8]. Na₂¹¹B₁₂H₁₂ was used for all pure Na₂B₁₂H₁₂ compound data presented. Natural-boron Na₂B₁₂H₁₂ was used to prepare a Na₂B₁₂H₁₂/Na₂B₁₀H₁₀ mixed compound. All compounds were dried under appropriate conditions of vacuum, time, and temperature [4,5,7,12]. The resulting anhydrous compounds were ball-milled using a Fritsch Pulverisette no. 7 planetary ball mill at 400 Hz. The total processing times were comprised of repetitive two-step sequences, which varied by material. Stainless steel vials (12 mL) with six 10 mm balls and six 1 mm balls per vial were typically used with sample masses of ~0.3–0.4 g.

Compounds before and after ball-milling were structurally characterized by X-ray powder diffraction (XRD) using a Rigaku Ultima III X-ray diffractometer with a Cu-K α source (λ = 1.5418 Å). Structural refinements were performed using the Fullprof software [17]. Various neutron scattering measurements of pristine and ball-milled Na2¹¹B12H12 were performed at the National Institute of Standards and Technology Center for Neutron Research. Quasielastic neutron scattering (QENS) measurements were taken on both the Disc Chopper Spectrometer (DCS) using incident neutrons of 12 Å wavelength (0.57 meV) with a full-width-at-half-maximum (fwhm) resolution of 11 µeV, and the High-Flux Backscattering Spectrometer (HFBS) using 6.27 Å neutrons with a fwhm resolution of 0.8 µeV. HFBS fixed-window scans were collected at ± 0.5 K min⁻¹ ramp rates. All neutron inelastic scattering data were analyzed using the DAVE software package [18]. Ionic conductivities were determined under Ar by the AC complex impedance method with a two-probe technique using an NF 5097 frequency response analyzer over a frequency range of 1 Hz to 10 MHz. The powder samples were pressed into pellets of 5 mm in diameter and approximately 2 mm in thickness without sintering. yielding densities typically more than 93% of those calculated from the lattice parameters. Au foils were used as electrodes for both Na₂B₁₂H₁₂ and Li₂B₁₂H₁₂ and mechanically fixed onto both faces of the pellets.

N.B., standard uncertainties for all figures in the text and Supplementary Material are commensurate with the observed scatter in the data, if not explicitly designated by vertical error bars.



Fig. 1. Room-*T* XRD data [experimental (blue circles), fitted (orange line), and difference (black line) patterns] for (a) pristine $Na_2B_{12}H_{12}$, (b) ball-milled $Na_2B_{12}H_{12}$, and (c) ball-milled 1:1 $Na_2B_{12}H_{12}$: $Na_2B_{10}H_{10}$. Red and green bars indicate the positions of Bragg peaks for the low-*T* monoclinic and high-*T* pseudo-bcc phases, respectively; refinement-derived phase fractions are listed. See Supplementary Material for more details. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

Fig. 1a and b depict representative X-ray powder diffraction (XRD) patterns for $Na_2B_{12}H_{12}$ before and after ball-milling for 72 h. (See Table S1 and Figs. S1-S8) for ball-milling details and corresponding XRD results for the other compounds studied.) As exemplified here, ball-milling introduces substantial Bragg peak broadening in all studied compounds. Moreover, phase analyses of the post-ball-mill patterns by Rietveld refinement are consistent with the presence of two phases in all cases, the expected low-T ordered phase plus what appears to be a higher-symmetry disordered phase matching that normally observed above the orderdisorder phase transition. For Na₂B₁₂H₁₂, the ordered phase has monoclinic symmetry, whereas the disordered phase has bodycentered-cubic (bcc) symmetry [7]. After ball-milling, the molar ratio of ordered-to-disordered phases was estimated from refinement to be 76:24. Complementary neutron powder diffraction (NPD) measurements (Fig. S9) confirmed that the disordered bcc fraction remained stable down to at least 5 K, and neutron vibrational spectra (Fig. S10) revealed minor phonon perturbations due to this disorder.

Fig. S11 displays representative scanning electron microscopy images of both $Na_2B_{12}H_{12}$ and $Li_2B_{12}H_{12}$ before and after ballmilling, elucidating the milling-induced particle pulverization. For all these materials, it is clear that increasing the fraction of superionic phase will depend on more aggressive milling conditions or more efficient and thorough ways to maximize the necessary nanoparticulate morphologies. For example, we noticed in our past investigations to create modified materials by infiltrating smaller anions into the polyhedral salt structures via ball-milling, that these additional salt compounds potentially acted as "abrasives" to enhance the particle-size reduction, leading to much higher fractions of disordered phase. This is exemplified in Fig. S6 by the XRD pattern for a 1:1 $Na_2B_{10}H_{10}$: Na_2CO_3 mixture ball-milled for 28 h, indicating that 82% of the $Na_2B_{10}H_{10}$ is in its disordered fcc phase at room temperature, compared with only around 27% after ball-milling for 80 h without any additive (Fig. S2). Differential scanning calorimetry (Fig. S12) confirmed no order-disorder phase transition upon cycling until the sample was annealed to ~550 K, presumably leading to increased particle sizes and reduced defects through accelerated sintering. This additive-assisted particle-size reduction was even observed at the lowest Na_2CO_3 doping of 5% and for other additives such as Na_2SO_4 .

Fig. 1c shows the room-*T* XRD pattern for a 1:1 mixture of $Na_2B_{12}H_{12}/Na_2B_{10}H_{10}$ after ball-milling for 4 h followed by vacuum annealing at 548 K for 16 h. This pattern is reminiscent of that for ball-milled $Na_2B_{12}H_{12}$ in Fig. 1b. Indeed, it is in line with the presence of both ordered monoclinic and disordered bcc solid-solution phases (each containing both $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ anions) with unit cell volumes intermediate between the ordered/disordered volumes of the pure compounds (see Fig. S7 for more details). Hence, this strongly suggests that nanocrystalline mixed-polyhedral-anion compounds can also be synthesized in this way, resulting in the room-*T* stabilization of their own disordered alloy phases.

Quasielastic neutron scattering measurements for the same pre- and post-ball-milled (11B-labeled) Na2B12H12 sample measured by XRD in Fig. 1 are shown in Fig. 2. The temperature behavior of the neutron fixed-window scans (FWSs) in Fig. 2a reflect ${B_{12}}{H_{12}}^{-2-}$ anion reorientational jump frequencies on the order of 10⁸ s⁻¹ already by \sim 240–250 K after ball-milling (as evidenced by the onset of more significant intensity dropoff), which is consistent with the presence of the high-T-like disordered phase manifested by XRD. In comparison, pristine Na₂B₁₂H₁₂ displays hysteretic FWS behavior and high reorientational mobility only at considerably higher temperatures, as expected [7]. QENS spectra of ball-milled Na2B12H12 were measured between 270 K and 400 K and could be fit to a primary Lorentzian component linewidth $(2\hbar)/\tau_1$, ranging between 0.27 µeV and 11 µeV fwhm, respectively. This narrow Lorentzian component dominated at lower Q values, with increasing contributions from one and probably more broader Lorentzian components at larger Q values, which is compatible with a small-angle jump mechanism [8]. Anion reorientational jump correlation frequencies derived from the QENS spectral broadening (Fig. 2b), are in excellent agreement with the Arrhenius dependence observed for pristine Na₂B₁₂H₁₂ above its phase transition at higher temperatures [8]. Combined data yield an activation energy for reorientation of 270(3) meV, the same value obtained for pristine bcc Na2B12H12 from NMR measurements [9].

The measured elastic fraction of the total QENS spectrum (i.e., the elastic incoherent structure factor, *EISF*) at 400 K at 0.84 Å⁻¹ (with 11 µeV resolution) was estimated to be ~0.48. Assuming a similar reorientational mechanism as for pristine disordered Na₂B₁₂H₁₂ [8], this *EISF* value is consistent with some small fraction (on the order of 20–25%) of the anions being relatively immobile in an ordered monoclinic phase at this temperature. Moreover the further decrease in the FWS in Fig. 2a upon heating above ~340 K indicates that this remaining "immobile" phase fraction converts to the superionic phase over a broad temperature range until its completion above 500 K. This transitioning fraction is reversible, as evidenced by the observed hysteretic FWS cooling behavior.

Since XRD results imply a much higher fraction of ordered phase, these dynamical results suggest that there is a significant fraction present of disordered amorphous or nanocrystalline phase invisible to diffraction and/or there are substantial contributions

Fig. 2. (a) Neutron fixed-window scans (HFBS, neutron momentum transfer Q=1.51 Å⁻¹) for Na₂B₁₂H₁₂ before (red) and after (blue) ball-milling for 72 h. Inset: QENS spectrum (348 K, Q=1.51 Å⁻¹) showing Lorentzian broadening (green) due to rapid anion reorientational motions ($\sim 3 \times 10^9$ jumps s⁻¹) for the ball-milled material. (b) Arrhenius plot of the jump correlation frequency (τ_1^{-1}) vs. T⁻¹ determined for ball-milled Na₂B₁₂H₁₂ (blue symbols) compared to τ_1^{-1} values for pristine Na₂B₁₂H₁₂ (N.B., red symbols; adapted from Ref. [8] τ^{-1} values, where $\tau_1^{-1}=0.5\tau^{-1}$). Squares and circles denote measurements on DCS and HFBS instruments, respectively. All data points fit well to a single line with a pre-exponential factor of 2.2(2) $\times 10^{13}$ s⁻¹ and an activation energy for reorientation F_a (from the *-E_a/k* slope) of 270(3) meV. (For interpretation of the sreferences to color in this figure legend, the reader is referred to the web version of this article.)

from "mobile" anions associated with a highly defective monoclinic phase. This is consistent with the NPD patterns for ballmilled Na₂B₁₂H₁₂ after the QENS measurements (see Fig. S9), which show a further increase in the crystalline bcc fraction, presumably from a slow coalescence of residual amorphous or nanocrystalline material during the (520 K maximum) FWS measurements. In addition, XRD patterns measured at elevated temperatures of 373 K and 438 K (not shown) indicated increasing fractions of bcc phase consistent with the reversible, temperaturedependent transformation of the immobile fraction seen in Fig. 2a. Even annealing at 620 K for 13 d led to a further increase in the apparent room-T fraction of bcc phase (see Fig. S8). One might speculate that minute fractions of the anions may be changing by both ball-milling and such elevated temperatures (e.g., by polymerization or degradation of the cage-like structure) and somehow act as morphology-stabilizing defects.

Fig. 3 compares the ionic conductivities of $Na_2B_{12}H_{12}$ pre- and post-ball-milling. Fig. S13 and S14 display the corresponding complex impedance and cyclic voltammetry plots of the ball-milled material. The post-ball-milling conductivities were evaluated after performing the QENS (Fig. 2) and NPD (Fig. S9) measurements. It is clear that this limited degree of ball-milling already leads to about a four-orders-of-magnitude conductivity





Fig. 3. Comparison of ionic conductivities for pristine [3] vs. ball-milled Na₂B₁₂H₁₂ after QENS measurements (see corresponding NPD patterns in Fig. S9). Closed and open symbols denote heating and cooling values, respectively. 1st, 2nd, and 3rd cycles: cyan, (\leq 373 K), green (\leq 423 K), and blue (\leq 573 K) symbols, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

enhancement compared with pristine Na₂B₁₂H₁₂ below its $T_{\rm trans}$ (and similar superionic conductivities above $T_{\rm trans}$). Further conductivity enhancements are expected with increasing bcc fraction. The conduction activation energy is 0.21 eV [3] for the pure superionic phase above ~480 K. Below this temperature, with respect to the ball-milled sample, the conductivity drops more rapidly with decreasing temperature, indicating that the activation energy is qualitatively larger in this mixed-phase region due to higher-barrier bottlenecks associated with the changing *T*-dependent fraction of ordered phase present.

Fig. S15 exemplifies the ionic conductivity behavior for Li₂B₁₂H₁₂ as a function of ball-milling time (i.e., disordered phase fraction), and Fig. S13 displays the related complex impedance plot. Again ball-milling dramatically enhances conductivity, and, indeed, more extensive ball-milling leads to further improvement. Yet, unlike Na₂B₁₂H₁₂, the morphology (and conductivity) for Li₂B₁₂H₁₂ is obviously affected after repeated temperature cycling to only 413 K. Thus, compared to Na₂B₁₂H₁₂, Li₂B₁₂H₁₂ appears to be less morphologically robust with respect to temperature. (This may well be a more general phenomenon concerning the relative morphological stabilities of Na and Li closo-borates, but this still needs to be resolved by further studies.) For Li₂B₁₂H₁₂ (and any other less morphologically robust compounds), it is likely essential to avoid excessively high temperatures or, e.g., resort to nanosequestration if one wants to effectively stifle sintering processes that would degrade lower-T conduction properties within the lifecycle of an all-solid-state energy storage device.

It is evident from the XRD, QENS, and AC impedance measurements that ball-milling these materials leads to room-T (and sub-room-T) stabilization of high-T-like disordered phases that typically only exist in the untreated bulk materials at more elevated temperatures. Although ball-milling-induced stresses and defects (vacancies, dislocations, stacking faults, grain boundaries, etc.) in the otherwise ordered room-T crystal structures may themselves lead to enhanced cation mobility, the likely stabilization of high-T-like superionic phases due to crystallite-size reduction into the nanoscale regime cannot be ignored. The atoms in any crystallite surface layer will reconstruct in such a way as to minimize the crystallite surface energy, which can often lead to non-bulk-like thermodynamic behavior for nanoscale crystallites, such as the adoption of a normally higher-*T* crystal structure [15] or a decrease in T_{trans} [19,20]. Although larger crystallites are dominated by their interior "bulk-like" region, the higher fraction of overall material associated with the surface of a polyhedral borate nanoparticle (which exhibits a large surface-to-bulk ratio as well as non-bulk-like finite-size effects) may translate into a higher fraction or complete stabilization of high-T-like disordered phase, if this phase has a lower surface energy. Compression of these powder materials would lead to a dense interconnecting conductive network of nanoparticles, allowing the cations to percolate through a continuum of facile pathways, even if these pathways are restricted to superionic nanoparticle surface layers surrounding more poorly conducting yet isolated crystallite interiors.

Lower-T conductivities resulting from pelletized, lightly ballmilled LiBH₄ were indeed reminiscent of the high values expected for its higher-T hexagonal (h) phase, but the broadened XRD pattern, was consistent with its low-T orthorhombic structure, with no clear evidence of a *h*-phase fraction [21]. This does not mean that the disorder and defects present in the material (particularly for nanosized particles and at the particle surfaces and grain boundaries) are not reflective of short-ranged hexagonal arrangements largely invisible to diffraction. Such nanoscale-driven modification, without the additional stresses and defects from ball-milling, is exemplified by the sequestration of LiBH₄ in nanoporous carbon and silica via melt-infiltration [20, 22-25]. In nanoporous carbon, NMR and QENS results [20,22,24] indicated two fractions of LiBH₄, a bulk-like fraction associated with the particle interiors and a more mobile fraction associated with the particle surface layers next to the pore walls. The latter fraction exhibited both enhanced BH4- anion reorientational and translational mobilities and Li⁺ cation translational mobility, and this fraction increased with decreasing pore size (over the investigated pore diameter range of \sim 25 nm to 2 nm). The enhanced ion mobilities observed at room temperature for LiBH₄ in both nanoporous carbon and silica were reminiscent of the presence of *h*-LiBH₄ [20,23], which is normally only stable above \sim 390 K. The more recent conductivity study [25] of LiBH₄ in nanoporous silica indeed reported lower T_{trans} values than for bulk LiBH₄ and *h*-phase-like fast-ion conduction down to room temperature, but the high ionic mobility was attributed to LiBH₄ likely near the pore interface, with no obvious phase transition. Again, this does not mean that this interface material was not also h-phase-like in character already at room temperature.

We note that particle-size reduction of a material by ball-milling or other means may not necessarily result in dramatically enhanced conductivity. There also must be a thermodynamic incentive to form an appropriately disordered phase, preferably one with cation vacancies. The nature of a material's high-*T* disordered structure may be a key predictor of its potential to form a room-*T*, nanocrystalline, fast-ion conductor. Also, for a bulk material that should hypothetically form a disordered structure, but is unable to do so due to decomposition or melting before attaining the necessary temperature, nanosizing may be a way to stabilize this otherwise unattainable or thermally unstable disordered structure. Indeed, Li₂B₁₂H₁₂ almost fits into this category, since its disordered phase is already rather unstable upon its formation above 615 K [7], whereas such a phase can be stabilized at much lower temperatures via ball-milling.

4. Conclusion

Pristine lithium and sodium salts with large polyhedral anion architectures have shown the capacity to form disordered phases with exceptional conductivities, yet only at somewhat elevated temperatures. These results clarify one strategy for stabilizing these superionic phases at room temperature and below. Crystal-lite-size-reduction processes such as ball-milling open the door for exploring further other possible superionic-phase-forming compounds based on this class of salts, including other cation substituents besides Li⁺ and Na⁺ and other related polyhedral anion substituents besides $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$, and $CB_{11}H_{12}^{-}$, regardless of their T_{trans} values. Moreover, new "alloy" compounds may result from ball-milling mixtures of these salts. Finally, the necessary nanosizing might also be accomplished in combination with or solely by other micronizing procedures such as spray drying or nanosequestration. These types of materials, with appropriate chemical and/or morphological modifications, merit further consideration as solid-state electrolyte materials in future energy-related devices.

Acknowledgments

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 the Collaborative Research Center on Energy Materials, 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 Nos. 25220911 and 26820311. This work used facilities supported, in part, by the NSF under Agreement No. DMR-0944772. The mention of all commercial suppliers in this paper and supplementary material is for clarity and does not imply the recommendation or endorsement of these suppliers by NIST.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ensm.2016.03.004.

References

[1] (a) M. Matsuo, S. Orimo, Adv. Energy Mater. 1 (2011) 161-172;

- (b) A. Unemoto, M. Matsuo, S. Orimo, Adv. Funct. Mater. 24 (2014) 2267–2279.
 [2] M. Matsuo, Y. Nakamori, S. Orimo, H. Maekawa, H. Takamura, Appl. Phys. Lett. 91 (2007) 224103.
- [3] T.J. Udovic, M. Matsuo, A. Unemoto, N. Verdal, V. Stavila, A.V. Skripov, J.J. Rush, H. Takamura, S. Orimo, Chem. Commun. 50 (2014) 3750–3752.
- [4] T.J. Udovic, M. Matsuo, W.S. Tang, H. Wu, V. Stavila, A.V. Soloninin, R. V. Skoryunov, O.A. Babanova, A.V. Skripov, J.J. Rush, A. Unemoto, H. Takamura, S. Orimo, Adv. Mater. 26 (2014) 7622–7626.
- [5] W.S. Tang, A. Unemoto, W. Zhou, V. Stavila, M. Matsuo, H. Wu, S. Orimo, T. J. Udovic, Energy Environ. Sci. 8 (2015) 3637–3645.
- [6] W.S. Tang, M. Matsuo, H. Wu, V. Stavila, W. Zhou, A.A. Talin, A.V. Soloninin, R. V. Skoryunov, O.A. Babanova, A.V. Skripov, A. Unemoto, S. Orimo, T.J. Udovic, Adv. Energy Mater. (2016), in press, http://dx.doi.org/10.1002/ aenm.201502237.
- [7] N. Verdal, J.-H. Her, V. Stavila, A.V. Soloninin, O.A. Babanova, A.V. Skripov, T. J. Udovic, J.J. Rush, J. Solid State Chem. 212 (2014) 81–91.
- [8] N. Verdal, T.J. Udovic, V. Stavila, W.S. Tang, J.J. Rush, A.V. Skripov, J. Phys. Chem. C 118 (2014) 17483–17489.
- [9] A.V. Skripov, O.A. Babanova, A.V. Soloninin, V. Stavila, N. Verdal, T.J. Udovic, J. J. Rush, J. Phys. Chem. C 117 (2013) 25961–25968.
- [10] A.V. Skripov, R.V. Skoryunov, A.V. Soloninin, O.A. Babanova, W.S. Tang, V. Stavila, T.J. Udovic, J. Phys. Chem. C 119 (2015) 26912–26918.
- [11] M. Paskevicius, M.P. Pitt, D.H. Brown, D.A. Sheppard, S. Chumphongphan, C. E. Buckley, Phys. Chem. Chem. Phys. 15 (2013) 15825–15828.
- [12] H. Wu, W.S. Tang, V. Stavila, W. Zhou, J.J. Rush, T.J. Udovic, J. Phys. Chem. C 119 (2015) 6481–6487.
- [13] J.A. Teprovich Jr., H. Colón-Mercado, A.L. Washington II, P.A. Ward, S. Greenway, D.M. Missimer, H. Hartman, J. Velten, J.H. Christian, R. Zidan, J. Mater, Chem. A 3 (2015) 22853–22859.
- [14] (a) J. Huot, G. Liang, S. Boily, A.V. Neste, R. Schulz, J. Alloy. Compd. 293–295 (1999) 495–500;
 - (b) H.G. Schimmel, M.R. Johnson, G.J. Kearley, A.J. Ramirez-Cuesta, J. Huot, F. M. Mulder, J. Alloy. Compd. 393 (2005) 1–4.
- [15] J.M. McHale, A. Auroux, A.J. Perrotta, A. Navrotsky, Science 277 (1997) 788–791.
- [16] R. Demir-Cakan, W.S. Tang, A. Darwiche, R. Janot, Energy Environ. Sci. 4 (2011) 3625–3631.
- [17] J. Rodriguez-Carvajal, Physica B 192 (1993) 55-69.
- [18] R.T. Azuah, L.R. Kneller, Y. Qiu, P.L.W. Tregenna-Piggott, C.M. Brown, J.R. D. Copley, R.M. Dimeo, J. Res. Natl. Inst. Stand. 114 (2009) 341–358.
- [19] A.F. Gross, J.J. Vajo, S.L. Van Atta, G.L. Olson, J. Phys. Chem. C 112 (2008) 5651–5657.
- [20] N. Verdal, T.J. Udovic, J.J. Rush, X. Liu, E.H. Majzoub, J.J. Vajo, A.F. Gross, J. Phys. Chem. C 117 (2013) 17983–17995.
- [21] D. Sveinbjörnsson, J.S.G. Myrdal, D. Blanchard, J.J. Bentzen, T. Hirata, M. Bjerg Mogensen, P. Norby, S. Orimo, T. Vegge, J. Phys. Chem. C 117 (2013) 3249–3257.
- [22] D.T. Shane, R.L. Corey, C. McIntosh, L.H. Rayhel, R.C. Bowman Jr., J.J. Vajo, A. F. Gross, M.S. Conradi, J. Phys. Chem. C 114 (2010) 4008–4014.
- [23] M.H.W. Verkuijlen, P. Ngene, D.W. de Kort, C. Barre, A. Nale, E.R.H. van Eck, P.J. M. van Bentum, P.E. de Jongh, A.P.M. Kentgens, J. Phys. Chem. C 116 (2012) 22169–22178.
- [24] X. Liu, E.H. Majzoub, V. Stavila, R.K. Bhakta, M.D. Allendorf, D.T. Shane, M. S. Conradi, N. Verdal, T.J. Udovic, S.-J. Hwang, J. Mater. Chem. A 1 (2013) 9935–9941.
- [25] D. Blanchard, A. Nale, D. Sveinbjörnsson, T.M. Eggenhuisen, M.H.W. Verkuijlen, Suwarno, T. Vegge, A.P.M. Kentgens, P.E. de Jongh, Adv. Funct. Mater. 25 (2015) 184–192.

Stabilizing Lithium and Sodium Fast-Ion Conduction in Solid Polyhedral-Borate Salts at Device-Relevant Temperatures

Wan Si Tang,^{a,b} Motoaki Matsuo,^c Hui Wu,^a Vitalie Stavila,^d Atsushi Unemoto,^e Shin-ichi Orimo,^{c,e} and Terrence J. Udovic^a

- ^a NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-6102, United States
- ^b Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2115, United States
- ^c Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
- ^d Energy Nanomaterials, Sandia National Laboratories, Livermore, CA 94551, United States
- ^e WPI-Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

The purpose of this communication is to demonstrate the proof of concept that, in general, ball-milling these large-anion *closo*-borate type salts leads to the room-T (and lower-T) stabilization of their high-T disordered phases, enabling enhanced conductivities at more device-relevant temperatures. Na₂B₁₂H₁₂ was used as an appropriate example in Figs. 1-3 since the differing XRD patterns of its ordered monoclinic and disordered pseudo-bcc phases are more easily distinguished from each other than the ordered- and disordered-phase patterns of the other materials studied. Yet, as is shown by the XRD results below, the stabilization of disordered high-T-like phases by ball-milling is indicated by Rietveld refinements for all the other materials studied (and at least suggested for Li₂B₁₀H₁₀, since its high-T structure is still unknown). It should be noted that we did not attempt to optimize the ball-milling process to maximize the formation of the disordered phases. Fig. 3 demonstrates that both ball-milled and pristine $Na_2B_{12}H_{12}$ have similar superionic conductivities above the pristine T_{trans} . Clearly, more aggressive milling conditions will enhance the disordered-phase fractions and lead to further conductivity improvements below the pristine T_{trans} , as demonstrated in Fig. S13. This optimization will be the goal of much more extensive future investigations. Moreover, except for some preliminary experiments with Li₂B₁₂H₁₂ and Na₂B₁₂H₁₂ reported in this communication, we did not undertake detailed thermal aging studies of the different materials to determine their relative resistances to reversion back to "pristine" structural behavior via sintering. The exemplary Li₂B₁₂H₁₂ and Na₂B₁₂H₁₂ results presented in this communication suggest that the sodium salts may be more morphologically robust compared to their lithium congeners, but more extensive experiments (beyond the scope of this study) are necessary to test this hypothesis.

Ball-Milling Treatments

Sample	Cycle Duration (min)		Total time (b)	Total milling
	BM	Pause	rotar time (ii)	time (h)
Na ₂ ¹¹ B ₁₂ H ₁₂	48	12	90	72
NaCB ₁₁ H ₁₂	30	5	100	86
$Na_2B_{10}H_{10}$	50	2	83	80
$Li_2B_{12}H_{12}$	2	0.5	20, 100	16, 80
LiCB ₁₁ H ₁₂	30	5	100	86
$Li_2B_{10}H_{10}$	48	12	100	80
Na ₂ B ₁₀ H ₁₀ :Na ₂ CO ₃ (1:1)	2	0.5	35	28
Na ₂ B ₁₂ H ₁₂ /Na ₂ B ₁₀ H ₁₀ (1:1)	2	0.5	4	3.2

Table S1. The ball-milling treatment conditions for the various samples investigated.

X-ray Powder Diffraction (XRD) Measurements

XRD patterns for the ball-milled materials all display line broadening compared to the pristine materials. Average crystallite sizes (absent any other line-broadening effects such as inhomogeneous strains and lattice imperfections) mentioned below were estimated from the Scherrer equation [1], $t \approx K\lambda/[\beta cos(\vartheta)]$, where t is the crystallite size (nm), K is the shape factor (rad, assumed to be 0.9), λ is the x-ray wavelength (0.15418 nm), β is the fwhm line broadening of the peak (rad), and ϑ is the Bragg angle (rad). As there is probably a very broad distribution crystallite coherency lengths, this should be considered as only a rough qualitative comparison of relative average crystallite sizes before and after ball-milling.

For the Na₂B₁₂H₁₂ XRD data in Fig. 1, the patterns were refined using the low-*T* monoclinic *P*2₁/*n* and high-*T* pseudo-bcc *Pm*-3*n* structures [2,3]. The refined unit cell parameters for the pristine sample are *a* = 7.0240(3) Å, *b* = 10.6426(5) Å, *c* = 7.0119(5) Å, β = 94.842(4)°, and *V* = 522.29(5) Å³ for the low-*T* structure (R_p = 0.152; R_{wp} = 0.170). The refined unit cell parameters for the ball-milled sample are *a* = 6.981(2) Å, *b* = 10.672(3) Å, *c* = 7.009(3) Å, β = 94.40(2)°, and *V* = 520.7(3) Å³ for the low-*T* structure; and *a* = 7.963(2) Å and *V* = 505.0(2) Å³ for the high-*T* structure (R_p = 0.122; R_{wp} = 0.131). The insets compare the relative line-broadening of the main peaks pre- and post-ball-milling. From the Scherrer equation, the particle size of the monoclinic-structured crystallites is estimated as 39 nm before ball-milling, decreasing to 13 nm after ball-milling.



Figure S1. Room-*T* XRD data [experimental (blue circles), fitted (orange line), and difference (black line) patterns] for (a) pristine and (b) ball-milled NaCB₁₁H₁₂. Vertical red and green bars indicate the positions of Bragg peaks for the low-*T* (*Pca*2₁) orthorhombic and high-*T* (*Fm*-3*m*) face-centered-cubic (fcc) phases, respectively [4]. The refined unit cell parameters for the pristine sample are a = 9.7821(4) Å, b = 9.6254(4) Å, c = 10.0928(4) Å, and V = 950.30(6) Å³ for the low-*T* structure ($R_p = 0.091$; $R_{wp} = 0.093$). The refined unit cell parameters for the ball-milled sample are a = 9.8192(6) Å, b = 9.6868(5) Å, c = 10.1159(5) Å, and V = 962.18(9) Å³ for the low-*T* structure; and a = 9.9065(5) Å and V = 972.20(8) Å³ for the high-*T* structure ($R_p = 0.145$; $R_{wp} = 0.129$). The insets compare the relative line-broadening of the main peaks pre- and post-ball-milling. From the Scherrer equation, the particle size of the orthorhombic-structured crystallites is estimated as 44 nm before ball-milling, decreasing to 26 nm after ball-milling.



Figure S2. Room-*T* XRD data [experimental (blue circles), fitted (orange line), and difference (black line) patterns] for (a) pristine and (b) ball-milled Na₂B₁₀H₁₀. Vertical red and green bars indicate the positions of Bragg peaks for the low-*T* (*P*2₁/*c*) monoclinic and high-*T* (*Fm*-3*m*) fcc phases, respectively [5,6]. The refined unit cell parameters for the pristine sample are *a* = 6.7263(4) Å, *b* = 13.1520(8) Å, *c* = 11.9671(6) Å, β = 120.623(3)°, and *V* = 911.02(9) Å³ for the low-*T* structure (*R*_p = 0.127; *R*_{wp} = 0.134). The refined unit cell parameters for the ball-milled sample are *a* = 6.702(1) Å, *b* = 13.189(3) Å, *c* = 11.995(2) Å, β = 120.508(9)°, and *V* = 913.5(3) Å³ for the low-*T* structure; and *a* = 9.817(2) Å and *V* = 945.9(3) Å³ for the high-*T* structure (*R*_p = 0.180; *R*_{wp} = 0.177). The insets compare the relative line-broadening of the main peaks pre- and post-ball-milling. From the Scherrer equation, the particle size of the monoclinic-structured crystallites is estimated as 32 nm before ball-milling, decreasing to 23 nm after ball-milling.



Figure S3. Room-*T* XRD data [experimental (blue circles), fitted (orange line), and difference (black line) patterns] for (a) pristine, (b) 16 h ball-milled, and (c) 80 h ball-milled Li₂B₁₂H₁₂. Vertical red and green bars indicate the positions of Bragg peaks for the low-*T* (*Pa*-3) cubic and high-*T* (*Fm*-3*m*) fcc phases, respectively [2,7,8]. The refined unit cell parameters for the pristine sample are a = 9.5678(2) Å and V = 875.87(3) Å³ for the low-*T* structure ($R_p = 0.158$; $R_{wp}=0.179$). The refined unit cell parameters for the 16 h ball-milled sample are a = 9.5953(5) Å and V = 883.45(8) Å³ for the low-*T* structure; and a = 9.7230(9) Å and V = 919.17(15) Å³ for the high-*T* structure ($R_p = 0.065$; $R_{wp} = 0.068$). The refined unit cell parameters for the 80 h ball-milled sample are a = 9.5914(5) Å and V = 882.36(8) Å³ for the low-*T* structure; and a = 9.7482(7) Å and V = 926.4(1) Å³ for the high-*T* structure ($R_p = 0.106$; $R_{wp} = 0.106$; $R_{wp} = 0.110$). The insets compare the relative line-broadening of the main peaks pre- and post-ball-milling. From the Scherrer equation, the particle size of the low-*T*-cubic-structured crystallites is estimated as 49 nm before ball-milling, decreasing to 15 nm after 16 h of ball-milling and 13 nm after 80 h of ball-milling.



Figure S4. Room-*T* XRD data [experimental (blue circles), fitted (orange line), and difference (black line) patterns] for (a) pristine and (b) ball-milled LiCB₁₁H₁₂. Vertical red and green bars indicate the positions of Bragg peaks for the low-*T* (*Pca*2₁) orthorhombic and high-*T* (*Fm*-3*m*) fcc phases, respectively [4]. The refined unit cell parameters for the pristine sample are *a* = 9.6668(5) Å, *b* = 9.4892(5) Å, *c* = 9.7273(5) Å, and *V* = 892.28(8) Å³ for the low-*T* structure (*R*_p = 0.143; *R*_{wp} = 0.155). The refined unit cell parameters for the ball-milled sample are *a* = 9.678(1) Å, *b* = 9.537(1) Å, *c* = 9.7564(9) Å, and *V* = 900.5(2) Å³ for the low-*T* structure; and *a* = 9.734(1) Å and *V* = 922.4(2) Å³ for the high-*T* structure (*R*_p = 0.105; *R*_{wp} = 0.106). The insets compare the relative line-broadening of the main peaks pre- and post-ball-milling. From the Scherrer equation, the particle size of the orthorhombic-structured crystallites is estimated as 45 nm before ball-milling, decreasing to 15 nm after ball-milling.



Figure S5. Room-*T* XRD patterns for (a) pristine and (b) ball-milled Li₂B₁₀H₁₀. Experimental (blue circles), fitted (orange line) and difference (black line) are shown for the pristine sample. Vertical red bars indicate the positions of Bragg peaks for the low-*T* (*P*6₄22) hexagonal phase [9]. There is clearly disorder present in the ball-milled material, although its structure is still not established. The refined unit cell parameters for the pristine sample are *a* = 7.0416(4) Å, *c* = 14.9266(7) Å, and *V* = 640.97(6) Å³ for the low-*T* structure (*R*_p = 0.140; *R*_{wp} = 0.141). The significant peak broadening, amorphous background, and unknown structure of the high-*T*-disordered phase prevents any analysis by Rietveld refinement. The generated pattern (orange dotted line) for the ball-milled sample (for a possible hexagonal disordered phase) is based on the low-T hexagonal structure, but with modified unit cell parameters of a = 6.92 Å, *c* = 15.30 Å, and *V* = 634.5 Å³. The significant expansion along the c-direction would be consistent with the space needed to accommodate fully orientationally disordered B₁₀H₁₀²⁻ anions. The insets compare the relative line-broadening of the main peaks pre- and post-ball-milling. After ball-milling, the positions of the four main Bragg peaks are shifted as seen from the red dashed line (pristine) to the red dotted line (after ball-milling).



Figure S6. Room-T XRD data [experimental (blue circles), fitted (orange line), and difference (black line) patterns] for (a) pristine Na₂B₁₀H₁₀, (b) ball-milled 1:1 Na₂B₁₀H₁₀:Na₂CO₃, and (c) pristine Na₂CO₃. Vertical red and green bars indicate the positions of Bragg peaks for the low-T $(P2_1/c)$ monoclinic and high-T (Fm-3m) fcc Na₂B₁₀H₁₀ phases, respectively; purple bars indicate those for (C2/m) monoclinic Na₂CO₃ [10]. The refined unit cell parameters for the pristine Na₂B₁₀H₁₀ sample are a = 6.7263(4) Å, b = 13.1520(8) Å, c = 11.9671(6) Å, $\beta = 120.623(3)^{\circ}$, and V = 911.02(9) Å³ for the low-*T* structure (R_p = 0.127; R_{wp} = 0.134) (*cf.* Fig. S2a). The refined unit cell parameters for the ball-milled 1:1 Na₂B₁₀H₁₀:Na₂CO₃ sample are a = 6.795(2) Å, b = 13.294(4) Å, c = 11.988(4) Å, $\beta = 121.70(2)^{\circ}$, and V = 921.4(5) Å³ for the low-T Na₂B₁₀H₁₀ structure; a =9.7608(3) Å and V = 929.94(5) Å³ for the high-T Na₂B₁₀H₁₀ structure; and a = 8.9101(2) Å, b =5.2413(1) Å, c = 6.0461(1), and $\beta = 101.304(2)^{\circ}$ for Na₂CO₃ ($R_{p} = 0.115$; $R_{wp} = 0.116$). The refined unit cell parameters for the pristine Na₂CO₃ sample are a = 8.9114(2) Å, b = 5.2423(1) Å, c =6.0454(2), and $\beta = 101.339(1)^{\circ}$ ($R_{p} = 0.162$; $R_{wp} = 0.179$). The insets compare the relative linebroadening of the main peaks pre- and post-ball-milling. From the Scherrer equation, the particle size of the monoclinic-structured Na₂B₁₀H₁₀ crystallites is estimated as 32 nm before ball-milling, decreasing to 21 nm after ball-milling.



Figure S7. Room-T XRD data [experimental (blue circles), fitted (orange line), and difference (black line) patterns] for (a) ball-milled Na₂B₁₂H₁₂ and (b) a 1:1 Na₂B₁₂H₁₂:Na₂B₁₀H₁₀ mixture ballmilled for 3.2 h followed by vacuum annealing at 548 K for 16 h. Vertical red and green bars indicate the positions of Bragg peaks for the low-T ($P2_1/n$) monoclinic and high-T (Pm-3n) pseudo-bcc phases, respectively. The similarity of the mixed-compound pattern to that for Na₂B₁₂H₁₂ strongly suggests the presence of similar ordered monoclinic and disordered bcc solid-solution phases for the mixed compound (each containing both B₁₂H₁₂²⁻ and B₁₀H₁₀²⁻ anions), but with slightly smaller lattice constants than for pure Na₂B₁₂H₁₂. The refined unit cell parameters for the ball-milled Na₂B₁₂H₁₂ sample are a = 6.981(2) Å, b = 10.672(3) Å, c = 7.009(3)505.0(2) Å³ for the high-T structure ($R_p = 0.122$; $R_{wp} = 0.131$) (cf. Fig. 1b). Assuming similar low-T and high-T Na₂B₁₂H₁₂ structures but with average B and H site occupancies of 11/12, the refined unit cell parameters for the ball-milled Na₂B₁₂H₁₂:Na₂B₁₀H₁₀ sample are a = 6.882(3) Å, b =10.477(5) Å, c = 6.927(3) Å, $\beta = 91.9(3)^{\circ}$, and V = 499.1(4) Å³ for the low-*T* structure; and $a = 10.477(5)^{\circ}$ 7.8333(1) Å and V = 480.6(2) Å³ for the high-T structure ($R_p = 0.112$; $R_{wp} = 0.098$). These cell volumes are intermediate between those for Na₂B₁₂H₁₂ and Na₂B₁₀H₁₀, which is consistent with the formation of a solid-solution mixed-anion phase.



Figure S8. Room-*T* XRD data [experimental (blue circles), fitted (orange line), and difference (black line) patterns] for ball-milled Na₂B₁₂H₁₂ after annealing at 620 K for 13 d. Vertical red and green bars indicate the positions of Bragg peaks for the low-*T* (*P*2₁/*n*) monoclinic and high-*T* (*Im*-3*m*) bcc phases, respectively. The fully disordered *Im*-3*m* bcc structure [2] (instead of the intermediate pseudo-bcc *Pm*-3*n* structure) indexed best with the observed pattern. The refined unit cell parameters are *a* = 7.033(5) Å, *b* = 10.641(6) Å, *c* = 7.013(3) Å, β = 94.61(5) °, and *V* = 523.1(5) Å³ for the low-*T* monoclinic structure; and *a* = 7.938(2) Å and *V* = 500.3(2) Å³ for the high-*T* bcc structure (R_p = 0.177; R_{wp} = 0.154). As shown by the NPD data in Fig. S9, this indicates that the stabilized bcc phase for Na₂B₁₂H₁₂ increases upon annealing, even at 620 K, and is surprisingly robust with respect to temperature. Although not evaluated under these treatment conditions, it is likely that the ionic conductivity will be further enhanced with respect to that in Fig. 3.



Figure S9. NPD patterns [BT-1 Powder Diffractometer, Ge(311) mono., λ =2.079 Å] for Na₂¹¹B₁₂H₁₂: (a) at 5 K after ball-milling for 72 h and annealing at 410 K for 12 h. The bimodal feature represents the Bragg scattering from the ordered monoclinic (at lower angle) and disordered bcc (at higher angle) phases. Fig. S10 compares the 4 K neutron vibrational spectrum for this material at this thermal treatment stage with that for pristine Na₂¹¹B₁₂H₁₂. Subsequently, the neutron fixed-window scans (FWSs) and QENS data in Fig. 2 were collected up to 520 K. More NPD patterns were then collected at (b) 40 K, (c) 300 K, and (c) 520 K, indicating an increased bcc-phase fraction compared to (a) and an increasing bcc-phase fraction with temperature, in line with the FWS behavior in Fig. 2. The conductivity data in Fig. 3 was finally collected at this stage.





Figure S10. Neutron vibrational spectra at 4 K of Na₂¹¹B₁₂H₁₂ before and after ball-milling for 72 h and annealing at 410 K for 12 h (using the Filter-Analyzer Neutron Spectrometer [11] with the Cu(220) monochromator) compared to the simulated one-phonon (brown) and one+two-phonon (black) densities of states from DFT phonon calculations [3] of the optimized ordered monoclinic structure. (N.B., 1 meV \approx 8.066 cm⁻¹.) The disordered ball-milled sample displays some minor but clear perturbations of some anion internal-vibration bands compared to pristine monoclinic Na₂¹¹B₁₂H₁₂.

Scanning Electron Microscopy (SEM) Measurements



Figure S11. SEM images (using the JEOL JSM6009) of (a) pristine $Na_2B_{12}H_{12}$, (b) and (c) 72 h ballmilled $Na_2B_{12}H_{12}$ from the text, (d) pristine $Li_2B_{12}H_{12}$, and (e) and (f) 20 h ball-milled $Li_2B_{12}H_{12}$ from Fig. S15. After ball-milling, the particle size decreases to a few microns from 100-200 µm, and agglomeration occurs, as is often characteristic for the method.



Differential Scanning Calorimetry (DSC) Measurements







Figure S13. Symmetric-cell complex-impedance plots for ball-milled $Na_2B_{12}H_{12}$ and $Li_2B_{12}H_{12}$. The electrodes were mechanically fixed onto both pellet faces. The Na-symmetric-cell spectrum for ball-milled $Na_2B_{12}H_{12}$ consists of only a semi-circle due to contributions from the bulk and grain boundaries. On the other hand, for a Au-symmetric cell, a spike appears after the semi-circle in the low-frequency region caused by the electrode contribution. Similar behavior is observed for ball-milled $Li_2B_{12}H_{12}$ upon comparison of Li-symmetric and Au-symmetric cells.



Figure S14. Cyclic voltammetry data (at 5 mV/s) for ball-milled $Na_2B_{12}H_{12}$ sandwiched by Na and Mo electrodes at 303 K using a potentiostat/galvanostat (Princeton VersaSTAT4). Reversible Na deposition/stripping was observed nearly at 0 V, and no irreversible oxidation current appeared up to 5 V.



Figure S15. Comparative ionic conductivity plots for $Li_2B_{12}H_{12}$ vs. 1/T before (black) and after ball-milling for 10 min (blue) and 20 h (green). (N.B., this is a different $Li_2B_{12}H_{12}$ sample than shown in Fig. S3; corresponding XRD patterns in the inset again show evidence of increasing fraction of disordered phase with increasing ball-milling time, as in Fig S3). Solid lines denote the 1st heating runs. Dashed lines denote the 4th heating runs. Conductivities increase with ballmilling time. Reduced conductivities after repeated cycling to 413 K reflect the slow reversion back towards the original sample morphology. The conductivity decay of the pristine sample with increasing temperature above the 615 K order-disorder phase transition reflects the expected decomposition of the material at these temperatures. It is evident that the initial 10 min of ball-milling already generates enough superionic phase to increase the conductivity by an order of magnitude. Also, unlike for Na₂B₁₂H₁₂, it is clear that staying some distance below 413 K is required to inhibit $Li_2B_{12}H_{12}$ morphological reversion after ball-milling.

References

- [1] A.L. Patterson, Phys. Rev. 56 (1939) 978–982.
- [2] N. Verdal, J.-H. Her, V. Stavila, A.V. Soloninin, O.A. Babanova, A.V. Skripov, T.J. Udovic, J.J. Rush, J. Solid State Chem. 212 (2014) 81–91.
- [3] J.-H. Her, W. Zhou, V. Stavila, C.M. Brown, T.J. Udovic, J. Phys. Chem. C 113 (2009) 11187– 11189
- [4] W.S. Tang, A. Unemoto, W. Zhou, V. Stavila, M. Matsuo, H. Wu, S. Orimo, T.J. Udovic, Energy Environ. Sci. 8 (2015) 3637–3645.
- T.J. Udovic, M. Matsuo, W.S. Tang, H. Wu, V. Stavila, A.V. Soloninin, R.V. Skoryunov, O.A. Babanova, A.V. Skripov, J.J. Rush, A. Unemoto, H. Takamura, S. Orimo, Adv. Mater. 26 (2014) 7622–7626.
- [6] H. Wu, W.S. Tang, W. Zhou, V. Stavila, J.J. Rush, T.J. Udovic, CrystEngComm 17 (2015) 3533–3540.
- J.-H. Her, M. Yousufuddin, W. Zhou, S.S. Jalisatgi, J.G. Kulleck, J.A. Zan, S.-J. Hwang, R.C. Bowman, Jr., T.J. Udovic, Inorg. Chem. 47 (2008) 9757–9759.
- [8] M. Paskevicius, M.P. Pitt, D.H. Brown, D.A. Sheppard, S. Chumphongphan, C.E. Buckley, Phys. Chem. Chem. Phys. 15 (2013) 15825–15828.
- [9] H. Wu, W.S. Tang, V. Stavila, W. Zhou, J.J. Rush, T.J. Udovic, J. Phys. Chem. C 119 (2015) 6481–6487.
- [10] I. P. Swainson, M. T. Dove and M. J. Harris, J. Phys.: Condens. Matter, 1995, 7, 4395–4417.
- [11] T.J. Udovic, C.M. Brown, J.B. Leão, P.C. Brand, R.D. Jiggetts, R. Zeitoun, T.A. Pierce, I. Peral, J.R.D. Copley, Q. Huang, D.A. Neumann, R.J. Fields, Nucl. Instr. Meth. A 588 (2008) 406–413.