

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

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## 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.

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## 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-disorder-type phase transitions to fast-ion-conducting structures with orientationally mobile anions,  $LiBH_4$  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 complex-hydride-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],  $LiCB_{11}H_{12}$

[5],  $NaCB_9H_{10}$  [6], and  $LiCB_9H_{10}$  [6] with their overly large, cage-like anions exhibit exceptional ionic conductivities of  $\sim 0.1 \text{ S cm}^{-1}$  (540 K),  $0.01 \text{ S cm}^{-1}$  (383 K),  $0.12 \text{ S cm}^{-1}$  (383 K),  $0.15 \text{ S cm}^{-1}$  (403 K),  $0.05 \text{ S cm}^{-1}$  (323 K), and  $0.04 \text{ S cm}^{-1}$  (357 K), respectively, just above their phase transition temperatures  $T_{\text{trans}}$ . 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  $Li_2B_{12}H_{12}$  and  $Li_2B_{10}H_{10}$  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  $T_{\text{trans}}$  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  $Li_2B_{12}H_{12}$  study, which reported fast-ion conductivity at room temperature after only briefly milling the material, albeit at high energy [13]. This stabilization is not uncommon. Ball-milling of rutile  $MgH_2$ , e.g., leads to the low- $T$

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stabilization of high- $T$  orthorhombic  $\gamma$ -phase [14]. Corundum  $\alpha$ -phase  $\text{Al}_2\text{O}_3$  adopts the higher-entropy  $\gamma$ -phase polymorph when the crystallites are nanosized [15]. Finally,  $\text{Li}_3\text{N}$  is known to adopt its higher-pressure  $\beta$ -phase polymorph when confined inside carbon nanopores [16].

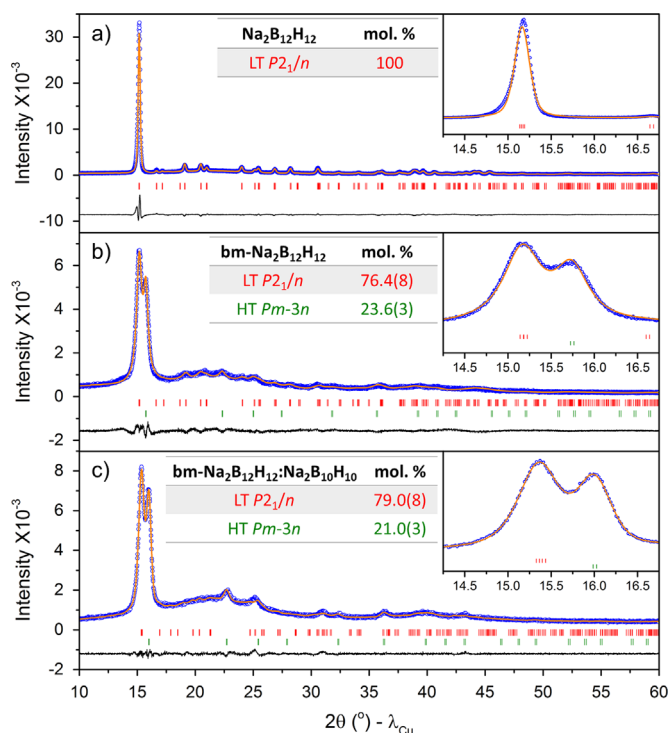
Here we report the room- $T$  stabilization, by ball-milling, of high- $T$ -like disordered phases for all lithium and sodium closo-borate compounds studied, namely:  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ ,  $\text{Li}_2\text{B}_{10}\text{H}_{10}$ ,  $\text{LiCB}_{11}\text{H}_{12}$ ,  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ ,  $\text{Na}_2\text{B}_{10}\text{H}_{10}$ , and  $\text{NaCB}_{11}\text{H}_{12}$ . Select AC impedance measurements for ball-milled  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  and  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  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

$\text{Li}_2\text{B}_{12}\text{H}_{12}$ ,  $\text{LiCB}_{11}\text{H}_{12}$ ,  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ ,  $\text{Na}_2\text{B}_{10}\text{H}_{10}$ , and  $\text{NaCB}_{11}\text{H}_{12}$  were obtained from Katchem.  $\text{Li}_2\text{B}_{10}\text{H}_{10}$  was synthesized as reported in Ref. [12].  $^{11}\text{B}$ -enriched  $\text{Na}_2^{11}\text{B}_{12}\text{H}_{12}$  (preferred for neutron scattering experiments) was prepared according to Ref. [8].  $\text{Na}_2^{11}\text{B}_{12}\text{H}_{12}$  was used for all pure  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  compound data presented. Natural-boron  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  was used to prepare a  $\text{Na}_2\text{B}_{12}\text{H}_{12}/\text{Na}_2\text{B}_{10}\text{H}_{10}$  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  $\sim 0.3$ – $0.4$  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  $\text{Cu-K}\alpha$  source ( $\lambda = 1.5418 \text{ \AA}$ ). Structural refinements were performed using the Fullprof software [17]. Various neutron scattering measurements of pristine and ball-milled  $\text{Na}_2^{11}\text{B}_{12}\text{H}_{12}$  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  $12 \text{ \AA}$  wavelength (0.57 meV) with a full-width-at-half-maximum (fwhm) resolution of  $11 \mu\text{eV}$ , and the High-Flux Backscattering Spectrometer (HFBS) using  $6.27 \text{ \AA}$  neutrons with a fwhm resolution of  $0.8 \mu\text{eV}$ . HFBS fixed-window scans were collected at  $\pm 0.5 \text{ K min}^{-1}$  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  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  and  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  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  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ , (b) ball-milled  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ , and (c) ball-milled 1:1  $\text{Na}_2\text{B}_{12}\text{H}_{12}:\text{Na}_2\text{B}_{10}\text{H}_{10}$ . 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  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  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 order-disorder phase transition. For  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ , the ordered phase has monoclinic symmetry, whereas the disordered phase has body-centered-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  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  and  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  before and after ball-milling, 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

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