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Sodium Superionic Conduction in $\text{Na}_2\text{B}_{12}\text{H}_{12}$

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Impedance measurements indicate that $\text{Na}_2\text{B}_{12}\text{H}_{12}$ exhibits dramatic Na^+ conductivity (on the order of 0.1 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 Nazar¹ and Hueso *et al.*² Sodium batteries based on Na-S and Na-NiCl₂ technologies^{3,4} have been commercially available for many years, typically employing a solid-state Na β '-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, $\text{Na}_2\text{B}_{12}\text{H}_{12}$, a complex hydride comprised of 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.

Figure 1 depicts the $\text{Na}_2\text{B}_{12}\text{H}_{12}$ low-temperature ordered monoclinic⁵ and high-temperature disordered, body-centered-cubic (bcc) phases.⁶ 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 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 α -phase of AgI,⁷ except that the preferred Ag^+ cation sites are believed to be in the center of the relatively smaller tetrahedral interstices of the bcc I sublattice. The similarities between the two systems suggested that a mobile "melted" 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 ²³Na NMR measurements of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ by Skripov *et al.*⁸ indicated an enhancement in the Na^+ cation jump rate to more than 2×10^8 jumps s^{-1} upon transformation to the high-temperature phase.

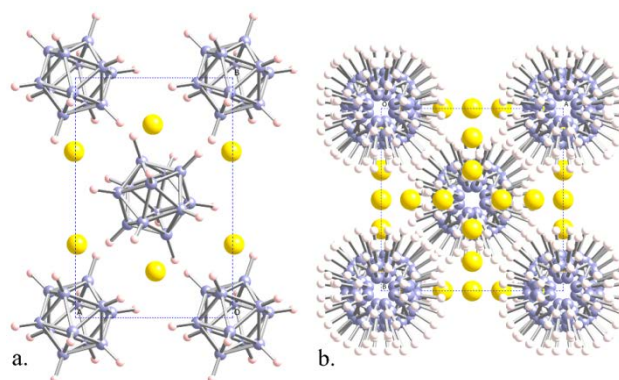


Fig. 1. Unit cells of the (a) low-temperature ordered monoclinic and (b) high-temperature disordered cubic $\text{Na}_2\text{B}_{12}\text{H}_{12}$ structures viewed along the a -axes. Yellow, purple, and white spheres represent Na, B, and H, respectively.

Based on the nature of the disordered $\text{Na}_2\text{B}_{12}\text{H}_{12}$ structure and the ²³Na 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.

Figure 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 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 $\approx 860 \text{ K}$.⁶ 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.⁶ 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.

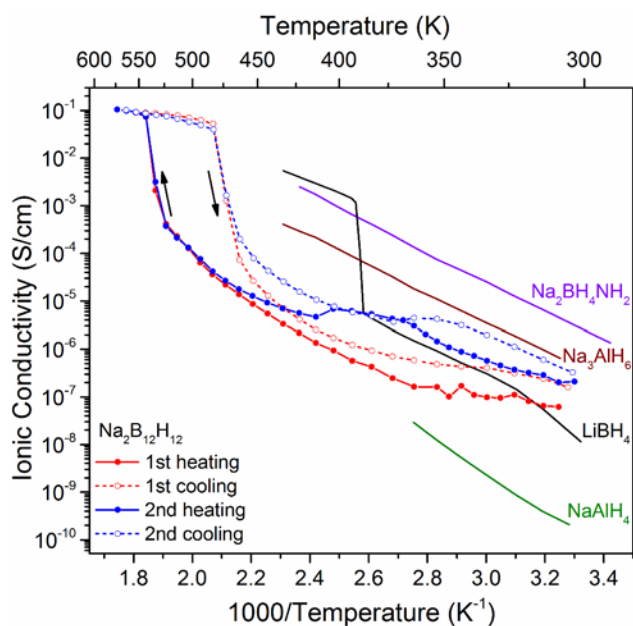


Fig. 2. Temperature dependence of the ionic conductivity of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ compared with that for other complex hydride materials: NaAlH_4 ,⁹ Na_3AlH_6 ,⁹ $\text{Na}_2\text{BH}_4\text{NH}_2$,¹⁰ and LiBH_4 .¹¹ Standard uncertainties are commensurate with the observed scatter in the data.

The complex impedance plots at various temperatures in Fig. 3 consist of an arc in the high-frequency range and a spike 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 AgI behavior¹² and indicates the profound advantage that disordered, cation-vacancy-rich structures such as cubic $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and AgI have over their lower-temperature ordered structures to facilitate fast conduction. This effect can also be seen in the conductivity behavior for LiBH_4 in Fig. 2, where the jump in Li

ion conductivity signals a phase change to a hexagonal structure with Li^+ cation disorder.^{13,14}

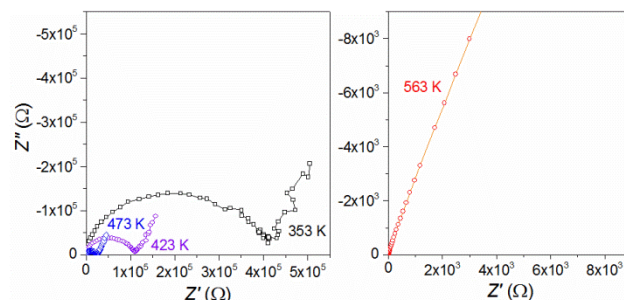


Fig. 3. Complex impedance plots of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ measured at various temperatures during heating run.

Visual extrapolation of the conductivity associated with cation-ordered NaAlH_4 and Na_3AlH_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 $\text{Na}_2\text{BH}_4\text{NH}_2$ structure¹⁵ 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.¹⁵

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, quasispherical $\text{B}_{12}\text{H}_{12}^{2-}$ 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 NaAlH_4 and Na_3AlH_6 , respectively,⁹ and 0.61(1) eV derived from the $\text{Na}_2\text{BH}_4\text{NH}_2$ conductivity data.¹⁰ 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 mechanism¹⁶ 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 $\text{Na}_2\text{B}_{12}\text{H}_{12}$, ^1H and ^{11}B NMR measurements⁸ indicate a nearly hundred-fold increase in the anion reorientational jump rate (to the order of $10^{11} \text{ jumps s}^{-1}$) upon reformation to the cubic phase. This is orders of magnitude higher than the observed Na^+ diffusional jump rate,⁸ suggesting that the rapidly spinning $\text{B}_{12}\text{H}_{12}^{2-}$ anions may indeed be acting as a “lubricant” for Na^+ 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 $\text{B}_{12}\text{H}_{12}^{2-}$ with other anions such as halides. This may have the secondary effect of also enhancing the Na^+ 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^+ , K^+ , or Mg^{2+} cations. For example, the recently reported disordered face-centered-cubic phase of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (Refs. 6, 17, 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 $\text{Na}_2\text{B}_{12}\text{H}_{12}$ has a somewhat high transition temperature, the two commercial solid-state Na battery systems are designed to operate above this temperature near 573 K.^{1,2} Since the conductivity of cubic $\text{Na}_2\text{B}_{12}\text{H}_{12}$ rivals that of Na β -alumina^{19,20} in this temperature region, it would be worth investigating the feasibility of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ 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.^{2,21}

In conclusion, we have shown that disordered cubic $\text{Na}_2\text{B}_{12}\text{H}_{12}$ displays dramatically high superionic conductivity, approaching and exceeding 0.1 S cm^{-1} 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 $\text{Na}_2\text{B}_{12}\text{H}_{12}$ 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^+ , K^+ , or Mg^{2+} cations are potentially fruitful additional systems to explore for favorable fast-ion conduction properties and also merit thorough investigations.

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Electronic Supplementary Information (ESI) available: $\text{Na}_2\text{B}_{12}\text{H}_{12}$ synthesis/stability and experimental details. See DOI: 10.1039/c000000x/

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