

Promoting Persistent Superionic Conductivity in Sodium Monocarba-*c*-closo-dodecaborate $\text{NaCB}_{11}\text{H}_{12}$ via Confinement within Nanoporous Silica

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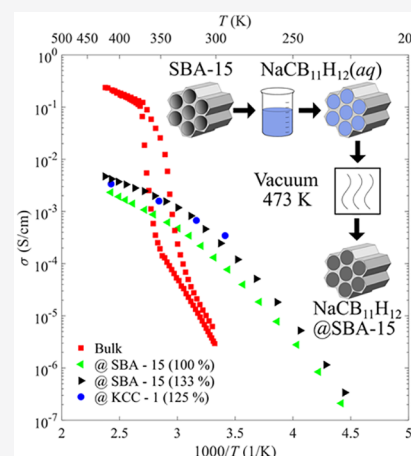
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ABSTRACT: Superionic phases of bulk anhydrous salts based on large cluster-like polyhedral (carba)borate anions are generally stable only well above room temperature, rendering them unsuitable as solid-state electrolytes in energy-storage devices that typically operate at close to room temperature. To unlock their technological potential, strategies are needed to stabilize these superionic properties down to subambient temperatures. One such strategy involves altering the bulk properties by confinement within nanoporous insulators. In the current study, the unique structural and ion dynamical properties of an exemplary salt, $\text{NaCB}_{11}\text{H}_{12}$, nanodispersed within porous, high-surface-area silica via salt-solution infiltration were studied by differential scanning calorimetry, X-ray powder diffraction, neutron vibrational spectroscopy, nuclear magnetic resonance, quasielastic neutron scattering, and impedance spectroscopy. Combined results hint at the formation of a nanoconfined phase that is reminiscent of the high-temperature superionic phase of bulk $\text{NaCB}_{11}\text{H}_{12}$, with dynamically disordered $\text{CB}_{11}\text{H}_{12}^-$ anions exhibiting liquid-like reorientational mobilities. However, in contrast to this high-temperature bulk phase, the nanoconfined $\text{NaCB}_{11}\text{H}_{12}$ phase with rotationally fluid anions persists down to cryogenic temperatures. Moreover, the high anion mobilities promoted fast-cation diffusion, yielding Na^+ superionic conductivities of ~ 0.3 mS/cm at room temperature, with higher values likely attainable via future optimization. It is expected that this successful strategy for conductivity enhancement could be applied as well to other related polyhedral (carba)borate-based salts. Thus, these results present a new route to effectively utilize these types of superionic salts as solid-state electrolytes in future battery applications.



INTRODUCTION

Since the first report of superionic conductivity observed in $\text{Na}_2\text{B}_{12}\text{H}_{12}$ above its order–disorder phase transition,¹ a rich variety of similarly superionic Li^+ , Na^+ , and Ag^+ solid-state electrolytes have been identified based on the anhydrous salts of the large cluster-like polyhedral (carba)borate anions.^{2–8} The critical factor promoting the superionic state is the formation of an entropy-driven disordered phase of rapidly reorienting anions among translationally fluidic interstitial cations, which normally occurs somewhere above room temperature, below which the ordered salt is poorly conductive. For practical battery applications, strategies are required to stabilize the superionic disordered phases at room temperature and below. Ball-milling these salts to create nanosized domains⁹ and combining salts with different polyhedral anions^{9–13} are two methods that have proven to be successful for stabilizing the desired disordered phases down to subambient temperatures. Here, we exemplify a third viable method, that is, the nanodispersion of polyhedral

(carba)borate salts within porous, high-surface-area silica (SiO_2) via salt-solution infiltration with subsequent vacuum desolvation. Somewhat analogous melt-infiltration of pure and anion-substituted LiBH_4 in nanostructured SiO_2 and Al_2O_3 has been shown to yield highly Li^+ -conductive nanocomposites.^{14–16}

In addition to these LiBH_4 -related examples, there have been at least two reported attempts to create similarly nanoconfined polyhedral (carba)borate salts, in particular, involving $\text{Li}_2\text{B}_{12}\text{H}_{12}$. In one case, further reaction of SBA-15 SiO_2 -nanoconfined LiBH_4 with an $\text{H}_2/\text{B}_2\text{H}_6$ gas mixture at 433 K was found to produce $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (with $\sim 6\%$ $\text{Li}_2\text{B}_{10}\text{H}_{10}$)

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within the (5.9 nm average diameter) cylindrical nanopores.¹⁷ Moreover, despite the apparently successful formation of a nanoconfined $\text{Li}_2\text{B}_{12}\text{H}_{12}$ reaction product, the resulting nanocomposite material displayed similarly low, ambient-temperature conductivities as bulk $\text{Li}_2\text{B}_{12}\text{H}_{12}$, reflecting the observed dominance within the nanopores of the ordered α - $\text{Li}_2\text{B}_{12}\text{H}_{12}$ phase that normally forms in the bulk at these temperatures. Despite this main ordered phase, the structural measurements could not rule out that a small fraction of the nanoconfined $\text{Li}_2\text{B}_{12}\text{H}_{12}$ was in its highly conductive, disordered β -phase. ^7Li nuclear magnetic resonance (NMR) also indicated the coexistence of temperature-independent fractions of more and less mobile Li^+ cations, although it is not clear to what extent the more mobile fraction is related to the presence of some β -phase and/or is associated with a perturbed $\text{Li}_2\text{B}_{12}\text{H}_{12}$ layer adjacent to the nanopore wall. In another subsequent study, it was found that solid crystalline adducts of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ with either acetonitrile (ACN) or tetrahydrofuran (THF) melt below 423 K during partial desolvation, and this allowed for the melt infiltration of $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot x\text{ACN}$ and $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot x\text{THF}$ into SBA-15 nanoporous SiO_2 .¹⁸ Further evacuation above ~ 493 K was suggested by X-ray diffraction techniques to yield nanoconfined, solvent-free, solidified $\text{Li}_2\text{B}_{12}\text{H}_{12}$, presumably with an α -phase signature. However, the resulting Li^+ conductivity behavior of a $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot x\text{THF}$ -derived nanocomposite was found to be unremarkable and akin to that of the previously reported¹⁷ impure $\text{Li}_2\text{B}_{12}\text{H}_{12}@\text{SiO}_2$ nanocomposites.

Unfortunately, these latter results do not firmly resolve whether nanoconfinement can help stabilize favorable non-bulk-like properties with enhanced Li^+ or other ion conductivities for any of the general class of polyhedral (carba)borate salts, as it has for LiBH_4 and its derivatives. We address this in the current study, where we turn our attention away from Li-based polyhedral (carba)borate salts and toward Na-based ones. In particular, sodium monocarba-closo-dodecaborate, $\text{NaCB}_{11}\text{H}_{12}$, was chosen in the present case based on its superior conductivity in the disordered state³ and its propensity to form highly concentrated aqueous solutions, which facilitates higher salt loadings within the pores during the salt-solution infiltration step.

EXPERIMENTAL DETAILS

$\text{NaCB}_{11}\text{H}_{12}$ was obtained from Katchem.¹⁹ Two morphologically distinct silica (SiO_2) scaffolds, shown schematically in Figure 1, were tested: (1) SBA-15 (Sigma Aldrich) hexagonal honeycomb arrays of nominally 8 nm diameter tubular nanopores (with a reported pore volume of $\sim 0.8\text{--}1.0\text{ cm}^3\text{ g}^{-1}$ and a surface area of $450\text{--}550\text{ m}^2\text{ g}^{-1}$) and (2) KCC-1 (Strem) high-surface-area ($700\text{ m}^2\text{ g}^{-1}$) spherical fibrous SiO_2 nanoparticles with interconnected nanoporous volume within the fiber network. Silica powders from the sealed vendor bottles were typically first evacuated at 473 K for 16 h to remove trace H_2O , although the lack of this step before infiltration was found not to affect the ultimate results. These powders were wetted at room temperature with chosen amounts of saturated aqueous $\text{NaCB}_{11}\text{H}_{12}$ solution (approximately 5.5 H_2O molecules per $\text{NaCB}_{11}\text{H}_{12}$ formula unit) using a micropipette. After stirring the slurry mixtures to ensure uniform infiltration via capillary action, H_2O was removed by vacuum evacuation at 473 K for 16 h. Additional anhydrous $\text{NaCB}_{11}\text{H}_{12}$ for comparative bulk measurements was also

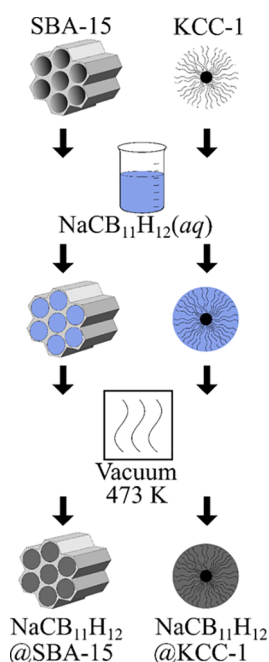


Figure 1. Schematic representation of the two nanostructures and the aqueous salt infiltration procedure.

generated using this drying procedure. After drying, all materials were handled in a He-filled glovebox.

Powder X-ray diffraction (PXRD) patterns were measured for each sample sealed in 1 mm diameter quartz capillaries at room temperature using a Rigaku Ultima III X-ray diffractometer with a $\text{Cu-K}\alpha$ source ($\lambda = 1.5418\text{ \AA}$). Differential scanning calorimetry (DSC) measurements with thermogravimetric analysis (TGA) were performed with a Netzsch (STA 449 F1 Jupiter) TGA–DSC under He flow using Al sample pans.

Low-field proton NMR measurements were performed on a pulse spectrometer described earlier²⁰ at the frequencies $\omega/2\pi = 14$ and 28 MHz. Typical values of the $\pi/2$ pulse length were 2–3 μs . High-field ^{23}Na NMR measurements were performed with a Bruker AVANCE III 500 spectrometer at the frequency $\omega/2\pi = 132.3$ MHz. Nuclear spin–lattice relaxation rates were measured using the saturation–recovery method. NMR spectra were recorded by Fourier-transforming the solid echo signals (pulse sequence $\pi/2_x - t - \pi/2_y$). NMR samples were flame-sealed in quartz tubes under vacuum.

Neutron scattering measurements were performed at the National Institute of Standards and Technology Center for Neutron Research using thin flat-plate-shaped samples to minimize neutron beam attenuation from the highly neutron-absorbing ^{10}B that comprises 20% of natural boron. Neutron vibrational spectroscopy (NVS) measurements were performed with the Filter-Analyzer Neutron Spectrometer (FANS)²¹ using a $\text{Cu}(220)$ monochromator with pre- and postcollimations of $20'$ of arc, yielding a full-width-at-half-maximum (FWHM) energy resolution of about 3% of the neutron energy transfer. Neutron-elastic-scattering fixed-window scans (FWSS) were performed between 120 and 420 K in heating and cooling regimes at $\pm 0.25\text{ K min}^{-1}$ with the High-Flux Backscattering Spectrometer (HFBS),²² which provides an energy resolution of 0.8 μeV FWHM using 6.27 \AA wavelength incident neutrons. Quasielastic neutron scattering (QENS) measurements were performed with the

DisKChopper Spectrometer (DCS),²³ utilizing incident neutron wavelengths of 8 Å (1.278 meV) and 10 Å (0.818 meV), with resolutions of 29.8 and 17 μ eV FWHM, respectively. QENS measurements below room temperature were performed using HFBS. The instrumental resolution functions on both instruments were obtained from the purely elastic QENS measurements at 4 K. Neutron data analyses were performed using the DAVE software package.²⁴

Alternating current (AC) impedance measurements were performed under a He atmosphere. The electrolyte powders were pressed into free-standing pellets with a diameter of 5 mm and thicknesses of about 2 mm. The pellets were formed under 250 MPa uniaxial pressure using a miniature button compression load cell from OMEGA and loaded into an MTI stainless steel cell with Au electrodes on both sides of the pellet. Once loaded, the MTI cell applies a pressure of approximately 2.7 MPa on the pellet. The measurements were performed at temperatures from 225 to 420 K using a closed-cycle He refrigerator. The sample temperature was measured using a calibrated thermocouple. The AC impedance spectra were collected from 1 Hz to 1 MHz using a VersaSTAT 4 potentiostat.

All structural depictions were made using the VESTA (visualization for electronic and structural analysis) software.²⁵ For all figures, standard uncertainties are commensurate with the observed scattering in the data, if not explicitly designated by vertical error bars.

RESULTS AND DISCUSSION

Pore Loading and Structural Characterization. DSC was used for establishing the maximum amount of NaCB₁₁H₁₂ that could be incorporated into the nanoporous silica structures via solution-loading because of the different calorimetric behaviors found for bulk and nanoconfined NaCB₁₁H₁₂. While bulk NaCB₁₁H₁₂ exhibits a reversible DSC peak (near 380 and 354 K upon heating and cooling, respectively) that reflects the enthalpic change occurring during its transition back and forth between its poorly conductive, ordered orthorhombic and superionic, disordered phases,³ nanoconfined NaCB₁₁H₁₂ was found to manifest no such enthalpic feature over the entire probed temperature range (100 to 473 K).

Samples loaded with different solution volumes (cm³) per gram of both SBA-15 and KCC-1 silica were prepared. DSC temperature-cycling measurements of the resulting dried nanocomposites lacked any observable enthalpic features for samples with solution loadings at or below ~ 0.9 and ~ 1.2 cm³ g⁻¹ for SBA-15 and KCC-1, respectively. In contrast, a bulk-like feature appeared for the higher-loading samples, with intensity increasing in a roughly linear fashion in proportion to the excess amount of solution added above the aforementioned values. An exemplary series of DSC scans for NaCB₁₁H₁₂@SBA-15 and NaCB₁₁H₁₂@KCC-1 in heating compared to that for bulk NaCB₁₁H₁₂ is shown in Figures 2 and S1, respectively. (Additional representative DSC cycling scans in both heating and cooling are shown in Figure S2.) These results suggest that all NaCB₁₁H₁₂ resides in the nanopores (exhibiting atypical NaCB₁₁H₁₂ calorimetric properties) after drying nanocomposites with solution loadings below these values. The cutoff at 0.9 cm³ g⁻¹ for SBA-15 is in line with its reported accessible pore volume; the higher 1.2 cm³ g⁻¹ cutoff for KCC-1 is also reasonable, considering its different morphology and associated 30–40% higher specific surface area compared to SBA-

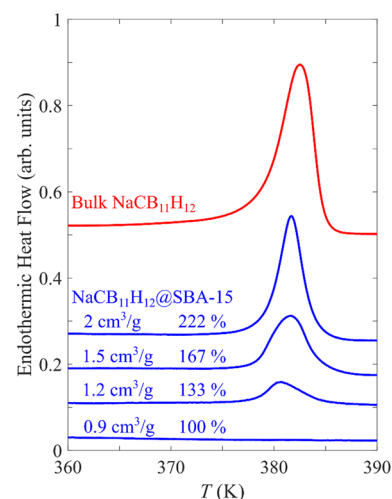


Figure 2. Exemplary DSC scans in heating (5 K min⁻¹) of dried NaCB₁₁H₁₂@SBA-15 nanocomposite samples derived from different saturated NaCB₁₁H₁₂ solution loadings (cm³ g⁻¹ and corresponding percentage of available pore volume filled) of SBA-15, compared with that for bulk NaCB₁₁H₁₂. All nanocomposite scans are normalized with respect to the same mass of SBA-15.

15, which is in agreement with the accessible KCC-1 pore volume reported by others.^{26,27} Henceforth, in subsequent discussion, we define 100% solution loading as 0.9 cm³ g⁻¹ for SBA-15 and 1.2 cm³ g⁻¹ for KCC-1.

Figure 3 shows the diffraction patterns for the ordered orthorhombic and disordered cubic and hexagonal phases of bulk NaCB₁₁H₁₂ compared with those for dried NaCB₁₁H₁₂@SiO₂ nanocomposites corresponding to various NaCB₁₁H₁₂ solution loadings in SBA-15. At 100% solution loading, the room-temperature pattern for the resulting nanosequestered NaCB₁₁H₁₂ displays one predominant, considerably broadened Bragg feature centered near 15.3°, which is in line with the main Bragg peak of the high-temperature face-centered-cubic (fcc) phase of bulk NaCB₁₁H₁₂ that was found to dominate at 356 K (with some remnant ordered orthorhombic phase).³ Moreover, there are indications of minor broad sidebands near 14.3 and 16.1°, which is consistent with the Bragg peak positions of two other higher-temperature polymorphs of bulk NaCB₁₁H₁₂ (with hexagonal symmetries) that were found to dominate at 428 K.³ Even the nonsymmetric shape surrounding the peak maximum may be an indication of an additional minor feature at 15.6°, which would match the fourth higher-temperature polymorph of bulk NaCB₁₁H₁₂ (with body-centered-cubic symmetry) that was also observed at 428 K.³ We note that the broadening of the peaks implies that the crystallites of NaCB₁₁H₁₂ are indeed nanosized, as expected.

For 110 and 140% loadings, on the top of the broadened Bragg feature, it is clear that additional sharp Bragg peaks representing the ordered orthorhombic phase of excess bulk NaCB₁₁H₁₂ outside the pores are present at room temperature and become more intense with increased loading. Moreover, as seen by the 400 K pattern for 110% loading, the sharp orthorhombic Bragg peaks for the excess bulk NaCB₁₁H₁₂ are replaced by the two expected peaks representing the high-temperature fcc phase, while little change is evident for the underlying broad Bragg feature because of the nanoconfined NaCB₁₁H₁₂. Analogous PXRD patterns for the KCC-1 infiltrated samples are exemplified in Figure S3. The results

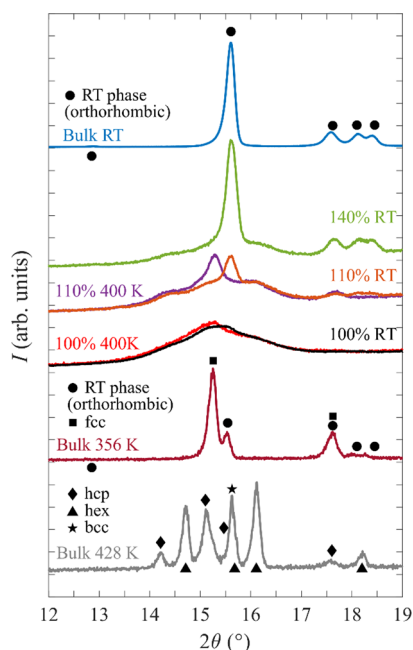


Figure 3. PXRD patterns for dried $\text{NaCB}_{11}\text{H}_{12}$ @SBA-15 nanocomposites for different solution loadings and measurement temperatures (100% loading, room temperature (RT): black; 100%, 400 K: red; 110%, RT: brown; 110%, 400 K: purple; and 140% RT: green) compared with bulk $\text{NaCB}_{11}\text{H}_{12}$ patterns (RT: blue, 356 K: maroon; and 428 K: gray) from a previous study.³ The Bragg positions of the bulk ordered orthorhombic phase are marked with black circles, whereas those for the various known disordered fcc, hcp, hexagonal, and bcc polymorphs are marked by black squares, diamonds, triangles, and stars, respectively.

are similar, although the fraction of the fcc polymorph in the pores appears to be lower than that in SBA-15 at the expense of the other known disordered polymorphs for $\text{NaCB}_{11}\text{H}_{12}$ highlighted in Figure 3. This is possibly due to a crystallite-size effect because the average pore size (as well as the pore size distribution) in KCC-1 has been shown to be larger than the distinct tubular 8 nm pores of SBA-15. Indeed, in addition to a minor fraction of smaller nanopores (<4–5 nm), the majority of the KCC-1 pore volume typically exists as mesopores ranging from roughly 5 nm to 25–30 nm.²⁶ This is consistent with the fact that the disordered polymorph PXRD features for $\text{NaCB}_{11}\text{H}_{12}$ @KCC-1 appear to be slightly sharper than those for $\text{NaCB}_{11}\text{H}_{12}$ @SBA-15, reflecting the larger average crystallite size for the former.

Neutron vibrational spectra at 4 K for bulk $\text{NaCB}_{11}\text{H}_{12}$ and both $\text{NaCB}_{11}\text{H}_{12}$ @SBA-15 and $\text{NaCB}_{11}\text{H}_{12}$ @KCC-1 (100% loadings) shown in Figure S4 indicate similar optical phonon densities of states characteristic of the various $\text{CB}_{11}\text{H}_{12}^-$ anion deformation modes.³ In short, the combined DSC, PXRD, and NVS results indicate that $\text{NaCB}_{11}\text{H}_{12}$ remains nanoconfined and undecomposed after drying the $\text{NaCB}_{11}\text{H}_{12}$ -solution-infiltrated SiO_2 . Moreover, although not conclusive, PXRD suggests the stabilization of room-temperature nanostructures similar to that of the disordered structures seen only at higher temperatures for bulk $\text{NaCB}_{11}\text{H}_{12}$. Because PXRD is only sensitive to ordered structures, we cannot rule out the existence of additional “invisible” amounts of amorphous-like $\text{NaCB}_{11}\text{H}_{12}$ within the pores, although the relative intensities of the Bragg features for bulk $\text{NaCB}_{11}\text{H}_{12}$ and disordered polymorphs in overloaded $\text{NaCB}_{11}\text{H}_{12}$ @ SiO_2 samples suggest

that the amount of any such amorphous material is very minor at best. Moreover, the preferred formation of normally higher-temperature, bulk-like polymorphs for nanoconfined $\text{NaCB}_{11}\text{H}_{12}$ at room temperature and below is not unexpected, as evidenced by the similar structural transformation of coarsely crystalline $\text{NaCB}_{11}\text{H}_{12}$ upon entering the nanocrystalline regime via ball-milling.⁹ The lack of an obvious DSC enthalpic feature down to 100 K further suggests that these nanostructures remain stable down to cryogenic temperatures. Finally, at higher solution loadings exceeding the accessible SiO_2 pore volume, both DSC and PXRD indicate that excess $\text{NaCB}_{11}\text{H}_{12}$ crystallizes outside the pore as bulk phase.

Anion and Cation Dynamics. The dynamical behaviors of the $\text{CB}_{11}\text{H}_{12}^-$ anions and Na^+ cations of the (100% loading) $\text{NaCB}_{11}\text{H}_{12}$ @SBA-15 SiO_2 nanocomposite were probed by ^1H and ^{23}Na NMR measurements to understand better the effects of nanoconfinement. Figure 4 shows the proton spin–lattice

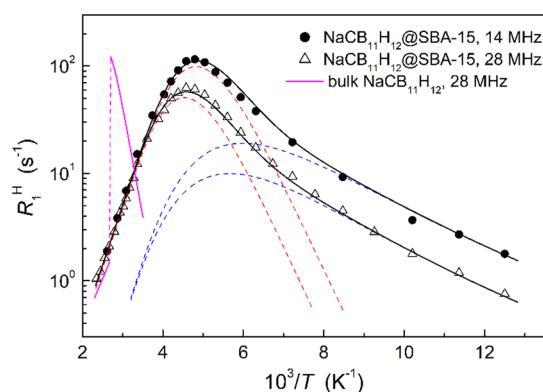


Figure 4. Proton spin–lattice relaxation rates measured at 14 and 28 MHz for $\text{NaCB}_{11}\text{H}_{12}$ @SBA-15 (100% loading) as functions of the inverse temperature. The black solid lines show the results of the simultaneous fit of a two-peak model to the data in the range 80–426 K. The dashed lines show the contributions of the faster (blue) and slower (red) jump processes to the fit. For comparison, the magenta lines show the behavior of the proton spin–lattice relaxation rate at 28 MHz in bulk $\text{NaCB}_{11}\text{H}_{12}$ (from ref 31).

relaxation rates, R_1^H , at $\omega/2\pi = 14$ and 28 MHz as functions of the inverse temperature. As in other polyhedral hydro(carba)-borate salts,²⁸ the behavior of R_1^H in $\text{NaCB}_{11}\text{H}_{12}$ @SBA-15 is governed by reorientations of the complex anions via the mechanism of motionally modulated dipole–dipole interactions between nuclear spins.²⁹ For this mechanism, $R_1^H(T)$ is expected to pass through a maximum at the temperature where the H jump rate τ^{-1} becomes nearly equal to the resonance frequency ω . For $\text{NaCB}_{11}\text{H}_{12}$ @SBA-15, this occurs at 210 K ($\sim 10^8 \text{ s}^{-1}$). It should be noted that the progression of the relaxation rate curve at lower temperatures shown in Figure 4 suggests the coexistence of an additional faster reorientational jump process, not unexpected based on the molecular symmetry of the dipolar $\text{CB}_{11}\text{H}_{12}^-$ anion. Indeed, a similar relaxation rate behavior reflecting coexisting jump processes was also observed for superionic $\text{Na}_2(\text{CB}_9\text{H}_{10})(\text{CB}_{11}\text{H}_{12})$, with the maximum in R_1^H occurring near 220 K for the orientationally disordered $\text{CB}_9\text{H}_{10}^-$ and $\text{CB}_{11}\text{H}_{12}^-$ anions in the hexagonal structure.^{10,30} This behavior for nanoconfined $\text{NaCB}_{11}\text{H}_{12}$ is in sharp contrast to that for bulk $\text{NaCB}_{11}\text{H}_{12}$, where $R_1^H(T)$ does not reach a maximum even upon heating to 376 K.³¹ Instead, the proton relaxation rate of bulk $\text{NaCB}_{11}\text{H}_{12}$ exhibits an abrupt two-orders-of-magnitude drop at 376 K, which relates

to the order–disorder phase transition, leading to the strong acceleration of the reorientational motion.³¹ The lack of such a rapid change in the jump rate points to the stabilization of bulk-like disordered phases down to cryogenic temperatures, which is in agreement with the DSC and PXRD results. In particular, the order–disorder phase transition normally occurring for bulk NaCB₁₁H₁₂ appears to be suppressed so that high reorientational mobility is retained down to low temperatures.

Figure 5 shows the measured ²³Na spin–lattice relaxation rate R_1^{Na} as a function of the inverse temperature. In the

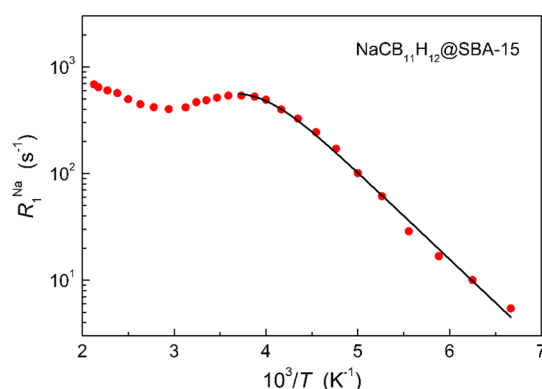


Figure 5. ²³Na spin–lattice relaxation rate measured at 132 MHz for NaCB₁₁H₁₂@SBA-15 (100% loading) as a function of the inverse temperature. The solid line shows the model fit (eq. S2 in the Supporting Information) to the data in the range 150–270 K.

temperature range 150–320 K, R_1^{Na} exhibits a behavior typical of the motionally induced spin–lattice relaxation with the characteristic peak near 270 K, indicating that the diffusive Na⁺ jump rate τ_d^{-1} reaches approximately $\omega \sim 8 \times 10^8 \text{ s}^{-1}$ at this temperature. An activation energy of 162(4) meV for the Na⁺ diffusive motion, E_a^d , was extracted by fitting the $R_1^{\text{Na}}(T)$ data in the temperature range 150–270 K; see Figure 5. Further details are given in the Supporting Information. In addition to the $R_1^{\text{Na}}(T)$ peak near 270 K, there is an increase in $R_1^{\text{Na}}(T)$ above 330 K, suggesting that there may be a second high-temperature relaxation rate peak, and thus, a second (slower) Na⁺ jump process may coexist with the faster Na⁺ jump process responsible for the $R_1^{\text{Na}}(T)$ peak near 270 K.

The evolution of the ¹H and ²³Na NMR line widths (Δ_{H} and Δ_{Na}) as a function of temperature for NaCB₁₁H₁₂@SBA-15 is shown in Figure 6. At low temperatures, Δ_{H} is determined by dipole–dipole interactions in the “rigid” lattice and is similar to the “rigid–lattice” Δ_{H} values ($\sim 50 \text{ kHz}$) of other polyhedral hydro(carba)borate salts.^{20,31} With increasing temperature, Δ_{H} starts to decrease because the dipole–dipole interactions between nuclear spins are partially averaged by the reorientational motion of the anions. A considerable decrease in Δ_{H} is expected when τ^{-1} becomes comparable to the “rigid–lattice” linewidth,²⁹ which can be seen to occur near 100 K for the NaCB₁₁H₁₂@SBA-15 nanocomposite. This indicates that the reorientational jump rate reaches $\sim 3 \times 10^5 \text{ s}^{-1}$ at this temperature. A typical feature of complex hydrides with reorienting anions is that Δ_{H} reaches a significant nonzero plateau value at higher temperatures.³² This indicates that the motion is a *localized* H motion (e.g., anion reorientations) because the dipole–dipole interactions of ¹H spins are not fully averaged by such motions, which leads to an offset.

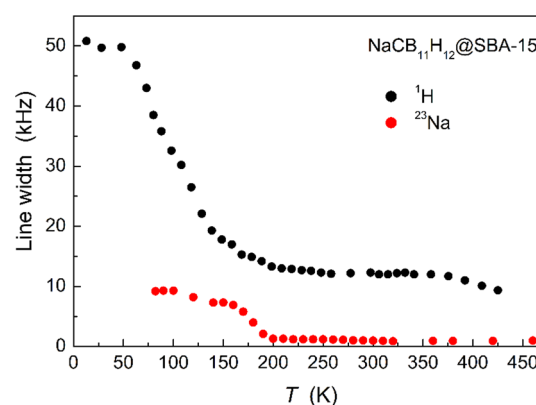


Figure 6. Temperature dependences of the ¹H and ²³Na NMR line widths (FWHM) measured for NaCB₁₁H₁₂@SBA-15 (100% loading) at 28 MHz (¹H) and 132 MHz (²³Na).

For Δ_{Na} , a strong narrowing near 180 K can be observed, indicating the onset of fast diffusive motion of Na⁺ cations with jump rates exceeding $\sim 10^4 \text{ s}^{-1}$. While the Δ_{H} high-temperature plateau value exhibits a significant offset, the Δ_{Na} high-temperature plateau value is close to zero ($\sim 0.95 \text{ kHz}$). This indicates that the Na⁺ cations participate in the *long-range* diffusion, which leads to an averaging out of both the dipole–dipole and quadrupole interactions of the ²³Na nuclei.

QENS measurements were conducted on the nanocomposites to examine the CB₁₁H₁₂[−] anion dynamics in further detail. In line with the NMR results, the nonhysteretic neutron-elastic-scattering FWSs for NaCB₁₁H₁₂@SBA-15 (100% loading) using HFBS (shown in Figure 7) indicate that anion reorientational jump rates enter the lower edge of the HFBS frequency window of $10^7 \text{ jumps s}^{-1}$ by $\sim 170 \text{ K}$, as signaled by the onset of a steeper drop in the elastic intensity above the more gradual Debye–Waller decay as the temperature is increased from 120 K. This steeper drop is a reflection

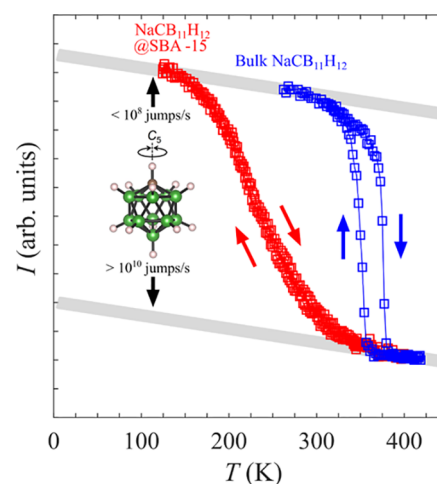


Figure 7. Neutron elastic-scattering FWS behavior for NaCB₁₁H₁₂@SBA-15 (100% loading) compared with that for bulk NaCB₁₁H₁₂.¹⁰ The gray lines indicate the decrease in the integrated FWS intensity related to the Debye–Waller factor summed over detectors covering a Q range of 0.87 to 1.68 Å^{−1}. Arrows differentiate heating and cooling scans. For a reasonable qualitative comparison, the individual data sets were scaled so as to have similar minimum and maximum intensities. Inset: reorienting CB₁₁H₁₂[−] anion with C, B, and H atoms denoted by brown, green, and white spheres, respectively.

of increasing quasielastic (Doppler-like) broadening of a portion of the elastic peak.³³ At room temperature, this quasielastic component becomes too broad to further affect the elastic intensity, and the elastic intensity starts to reflatten out in the Debye–Waller fashion, indicating that the jump rates for the nanoconfined anions now well exceed the order of 10^{10} jumps s^{-1} . Again, as hinted by the NMR results, the FWSs and underlying anion mobilities for $\text{NaCB}_{11}\text{H}_{12}@SBA-15$ are similar to those for the superionic $\text{Na}_2(\text{CB}_9\text{H}_{10})(\text{CB}_{11}\text{H}_{12})$ mixed-anion solid solution.¹⁰

It is clear from the heating and subsequent cooling scans for $\text{NaCB}_{11}\text{H}_{12}@SBA-15$ shown in Figure 7 that the anion mobilities exhibit nonhysteretic temperature dependence, which is consistent with the lack of any significant structural changes. This is in contrast to the hysteretic and sharper FWS decrease and increase observed for bulk $\text{NaCB}_{11}\text{H}_{12}$, which reflect the abrupt hysteretic order–disorder phase transformations between the lower-temperature, ordered orthorhombic structure (with anion jump rates $<10^7$ jumps s^{-1}) to the higher-temperature, disordered structures (with anion jump rates $>10^{10}$ jumps s^{-1}).

QENS spectra for both $\text{NaCB}_{11}\text{H}_{12}@SBA-15$ (100% loading) and $\text{NaCB}_{11}\text{H}_{12}@KCC-1$ (150% loading) typically consisted of a delta function (elastic scattering) and a Lorentzian function (quasielastic scattering), both convoluted with the instrumental resolution function above a flat baseline (Figure S6). The fundamental anion reorientational jump frequency τ_1^{-1} inferred by the FWSs was extracted from the Lorentzian quasielastic linewidth (FWHM) Γ at low Q (≤ 0.8 \AA^{-1}) as a function of temperature via the relation $\tau_1^{-1} = \Gamma/(2\hbar)$ and is shown in Figure 8 in comparison with that measured previously for bulk $\text{NaCB}_{11}\text{H}_{12}$.³⁴ As seen, the reorientational jump frequencies of the anions in the high-temperature disordered phase of bulk $\text{NaCB}_{11}\text{H}_{12}$ (red) and

both nanocomposites (blue and black) exhibit similar temperature-dependent behaviors above the bulk phase-transition temperature. This implies that SiO_2 -nanoconfined $\text{NaCB}_{11}\text{H}_{12}$ also possesses a bulk-like disordered structure in this temperature region. While the jump frequency decreases by two orders of magnitude for bulk $\text{NaCB}_{11}\text{H}_{12}$ upon cooling through the phase transition (indicated by the red arrows in Figure 8), the nanocomposite jump frequency, on the other hand, continues to extend its slower Arrhenius decrease to a low temperature, with a slope $[-E_a/k_B]$ based on the relationship $\tau_1^{-1} = \tau_0^{-1} \exp(-E_a/k_B T)$, where τ_0^{-1} , E_a , and k_B are the attempt frequency, activation energy, and Boltzmann constant, respectively] similar to the slope of the bulk $\text{NaCB}_{11}\text{H}_{12}$ jump frequency above its phase transition. In particular, the resulting activation energy for the combined $\text{NaCB}_{11}\text{H}_{12}@SBA-15$ and $\text{NaCB}_{11}\text{H}_{12}@KCC-1$ data over the broad temperature range of 235–410 K is 118(9) meV, which is in line with the 112 meV for bulk $\text{NaCB}_{11}\text{H}_{12}$ above the phase transition derived from previous QENS experiments.³⁴

We point out that the corresponding values of the activation energies obtained from proton NMR (as detailed in the Supporting Information) are 178 meV (the average activation energy for the faster reorientational jump process in $\text{NaCB}_{11}\text{H}_{12}@SBA-15$) and 177 meV (for the high- T disordered phase of bulk $\text{NaCB}_{11}\text{H}_{12}$).³¹ It should be noted that the activation energies derived from QENS measurements for a number of disordered phases of polyhedral hydro(carba)-borates appear to be somewhat lower than those resulting from proton NMR experiments. This feature is not uncommon, as explained in a previous study;²⁸ the most probable reason for such a systematic discrepancy is the presence of a certain distribution of H jump rates.

Figure 9 displays the Q -dependence of the elastic incoherent structure factor (EISF) for $\text{NaCB}_{11}\text{H}_{12}@SBA-15$ (100%

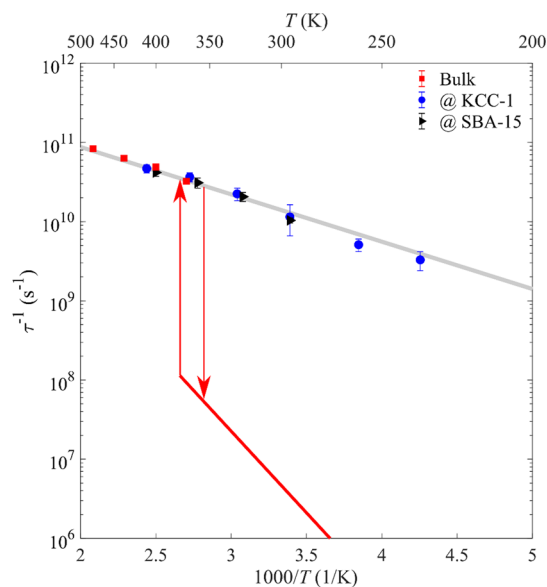


Figure 8. Anion reorientational jump frequencies τ_1^{-1} for $\text{NaCB}_{11}\text{H}_{12}$ nanoconfined in SBA-15 (100% loading) and KCC-1 (150% loading) compared with those for bulk $\text{NaCB}_{11}\text{H}_{12}$,³⁴ as determined by QENS. The red line shows the reorientational frequencies for the low-temperature phase of bulk $\text{NaCB}_{11}\text{H}_{12}$ determined by NMR,³¹ while the red arrows indicate the low-to-high/high-to-low phase-transition temperatures.

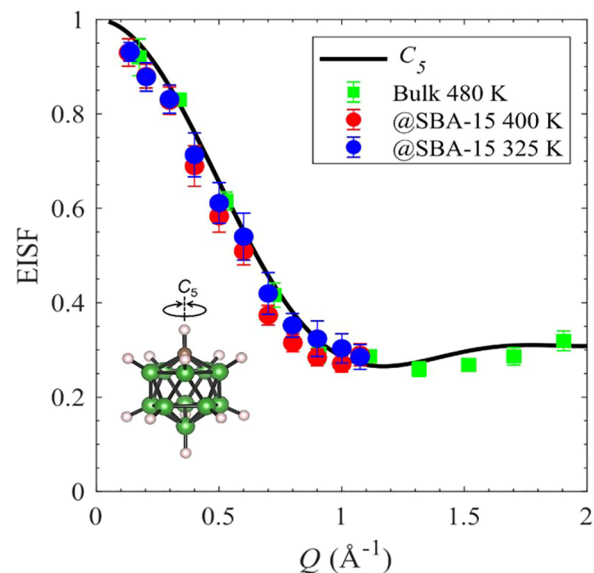


Figure 9. Comparison of the elastic incoherent structure factor (EISF) behavior for $\text{NaCB}_{11}\text{H}_{12}@SBA-15$ (100% loading) at 325 and 400 K with that previously reported for superionic disordered bulk $\text{NaCB}_{11}\text{H}_{12}$ at 480 K,³⁴ all shown to exhibit a Q -dependence that matches the specific model curve (black line) expected for uniaxial fivefold ($2\pi/5$) reorientational jumps around the $\text{CB}_{11}\text{H}_{12}^-$ anion C_5 symmetry axis³⁵ (see inset). Further model details can be found in the Supporting Information.

loading) at two temperatures (400 and 325 K, which are, respectively, above and below the bulk-phase-transition temperature), compared with that reported previously for superionic disordered bulk $\text{NaCB}_{11}\text{H}_{12}$ at 480 K.³⁴ The EISF is defined as the ratio of integrated neutron elastic scattering intensity to integrated total (elastic+quasielastic) scattering intensity (see Figure S6 in the Supporting Information for further details). The good agreement with the model curve shown in Figure 9 indicates that the $\text{CB}_{11}\text{H}_{12}^-$ anions in the disordered bulk $\text{NaCB}_{11}\text{H}_{12}$ preferentially undergo uniaxial fivefold ($2\pi/5$) reorientational jumps around the $\text{CB}_{11}\text{H}_{12}^-$ anion C_5 symmetry axis. It is also apparent that the anions in the nanoconfined $\text{NaCB}_{11}\text{H}_{12}$ follow this same C_5 model curve, both above and below the bulk order–disorder transition temperature. This not only further corroborates the dynamical similarities between the nanoconfined $\text{NaCB}_{11}\text{H}_{12}$ (over the entire temperature range probed) and bulk $\text{NaCB}_{11}\text{H}_{12}$ above its phase transition but also confirms that all $\text{CB}_{11}\text{H}_{12}^-$ anions in the nanoconfined $\text{NaCB}_{11}\text{H}_{12}$ remain highly mobile, even below the bulk phase-transition temperature. Indeed, any immobile, bulk-like fraction present in the nanopores would result in an anomalous increase in the measured EISF values at 325 K compared to those at 400 K and those for bulk $\text{NaCB}_{11}\text{H}_{12}$ at 480 K (Figure 9) because of an increased fraction of the elastic scattering intensity originating from such an immobile fraction.

The combined NMR and QENS dynamical results are in line with the PXRD structural results, all pointing to the stabilization of a disordered bulk-like phase for SiO_2 -nanoconfined $\text{NaCB}_{11}\text{H}_{12}$ over the entire studied temperature range, down to cryogenic temperatures.

Cationic Conductivity. The Na^+ ionic conductivities for three nanocomposites, $\text{NaCB}_{11}\text{H}_{12}$ @SBA-15 (100% and 133% loadings) and $\text{NaCB}_{11}\text{H}_{12}$ @KCC-1 (125% loading), are compared with those for bulk $\text{NaCB}_{11}\text{H}_{12}$ (Figure 10). For the bulk (red), two regions can be observed: a high-temperature region, where the sample is in its dynamically disordered phase with superionic conductivity ($\sim 1 \times 10^{-1} \text{ S cm}^{-1}$), and a low-temperature region, where the ionic conductivity is poor ($\sim 1 \times 10^{-5}$ – $1 \times 10^{-6} \text{ S cm}^{-1}$) because of the sample being in its ordered orthorhombic phase. Separating these two regimes is a phase-transition region where the conductivity changes drastically. The behavior of the nanoconfined $\text{NaCB}_{11}\text{H}_{12}$ (green, blue, and black) is utterly different; while the materials exhibit lower conductivities at higher temperatures ($\sim 2 \times 10^{-3}$ – $6 \times 10^{-3} \text{ S cm}^{-1}$), there is no pronounced drop at lower temperatures, and the conductivities remain relatively high at room temperature ($\sim 1 \times 10^{-4}$ – $3 \times 10^{-4} \text{ S cm}^{-1}$). This suggests that a highly conductive, dynamically disordered phase of $\text{NaCB}_{11}\text{H}_{12}$ was stabilized by the formation of the nanocomposite. Based on a linear least-squares fit of the plot of $\ln(\sigma T)$ vs T^{-1} shown in Figure S8 for the nanocomposite conductivity data (Figure 10) (133%-loaded SBA-15), a conductivity activation energy E_c of 216 meV was determined from the slope ($-E_c/k_B$) in the temperature range 330–420 K. Below 285 K, a second linear region can be observed with an activation energy of 567 meV. Separating these two regimes is a temperature-transition region (~ 285 – 300 K) where the slope gradually changes from the high-temperature value to the low-temperature value. This two-regime behavior and the corresponding temperature-transition region near the ambient temperature are similar to those observed previously for $\text{Na}_2(\text{CB}_9\text{H}_{10})(\text{CB}_{11}\text{H}_{12})$.¹⁰ Like

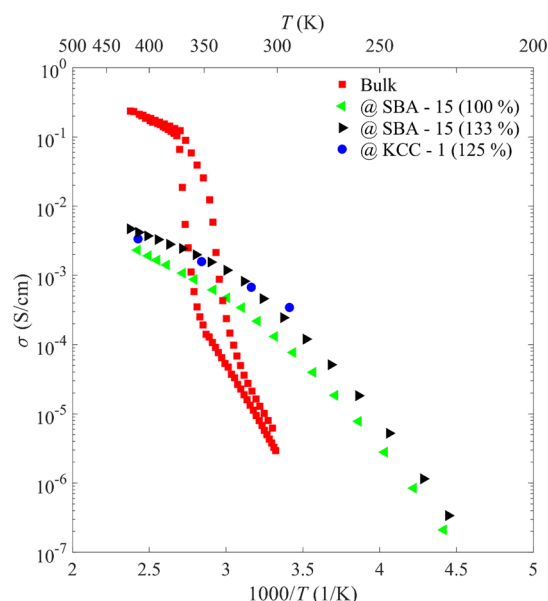


Figure 10. Na^+ cationic conductivities extracted from impedance spectroscopy for $\text{NaCB}_{11}\text{H}_{12}$ @SBA-15 (100 and 133% loading; green and black triangles) and $\text{NaCB}_{11}\text{H}_{12}$ @KCC-1 (125% loading; blue circles) as compared with those for bulk $\text{NaCB}_{11}\text{H}_{12}$ (red squares). In contrast to the hysteresis in conductivity observed for bulk $\text{NaCB}_{11}\text{H}_{12}$, none is evident for the nanocomposites. Representative Nyquist plots are shown in the Supporting Information, along with details for extracting the conductivities.

the *closo*-anions in this latter mixed-anion compound, the reorientational jump rate frequencies of the $\text{CB}_{11}\text{H}_{12}^-$ anions in $\text{NaCB}_{11}\text{H}_{12}$ @ SiO_2 in the temperature-transition region are of the order of 10^{10} jumps/s, which is only an order of magnitude or so higher than the translational jump frequencies of the Na^+ cations.^{30,31,36} Thus, although still significantly higher than the cation translational jump frequencies in this region, it is likely that further below these temperatures, the anion reorientational jump frequencies become too low and will no longer have such a marked synergistic dynamical effect³⁴ on the cation diffusion, as is the case at higher temperatures. This will ultimately lead to a change in the rate-limiting step, as reflected in the observed increase in E_c to 567 meV. It is worth pointing out that this activation energy for conductivity is significantly larger than that determined for Na^+ diffusion by NMR (162 meV) for this corresponding temperature region. However, this is reasonable and commonplace^{2,4} because the NMR value reflects the local (microscopic) conditions, while E_c reflects the global (macroscopic) conditions that include such additional effects as grain boundaries, pore-filling factors, and nanoparticle/cluster connectivity. The discrepancy in barriers indicates that E_c could potentially be improved to approach more closely the NMR value by addressing and mitigating the abovementioned global conductivity bottlenecks.

It should be noted that, although solution loadings above 100% shown here lead to dried nanocomposites with a minor amount of bulk $\text{NaCB}_{11}\text{H}_{12}$ crystallites outside the nanopores, the threefold poorer conductivities for 100%-loaded SBA-15 compared to 133%-loaded SBA-15 shown in Figure 10 indicate that some excess bulk $\text{NaCB}_{11}\text{H}_{12}$ is desirable to improve the ultimate ionic conductivities by presumably acting as a relatively thin bridge for enhancing the connectivity between otherwise contiguous clusters of the nanoconfined $\text{NaCB}_{11}\text{H}_{12}$.

material from different neighboring SiO₂ scaffold particles. Such a strategy was successfully used previously for nanoconfined LiBH₄ systems.¹⁵

In our studies, although increasing the loadings above the 100% level was found to benefit the conductivities above the bulk phase-transition temperature, above a certain point, it proved to be detrimental to the conductivities below the bulk-phase-transition temperature because of excessive amounts of poorly conductive bulk material separating neighboring SiO₂ particles. For example, we observed that increasing the loading of NaCB₁₁H₁₂@KCC-1 from 125 to 150% led to a similar favorable conductivity at 410 K (above the bulk phase-transition temperature) but a sixfold lower conductivity compared to that for 125% loading at room temperature (below the bulk phase-transition temperature).

Although it appears that the highly conductive, disordered NaCB₁₁H₁₂ phase is stabilized within the SiO₂ nanopores over a wide temperature range, it is also clear that various extraneous factors cause the ultimate conductivity of the pelletized nanocomposites to be more than an order of magnitude lower than that for bulk NaCB₁₁H₁₂ above its phase-transition temperature. In addition to the deleterious effect of incomplete conductive connectivity pathways that can occur between different infiltrated SiO₂ particles, the mere presence of the insulating SiO₂ scaffold material dilutes the otherwise conductive NaCB₁₁H₁₂, in effect, reducing the composite conductivity based on the overall cross-sectional area of the pellet. Also, because the infiltration method is solution-based instead of melt-based, the removal of the solvation water after 100% solution infiltration necessarily leaves about 40% void space in the dry-NaCB₁₁H₁₂-infused nanopores (based on saturated-solution and anhydrous NaCB₁₁H₁₂ densities), which likely causes further significant degradation in conductivity. Finally, the resulting pellet density after the compression of both SBA-15- and KCC-1-based samples is found to be roughly two times less than expected based on the densities of SiO₂ and NaCB₁₁H₁₂, which means that there is a substantial amount of extra void space accumulated between the SiO₂ scaffold particles, in addition to that formed within the nanopores from water removal. For example, assuming that the remaining nanopore void space stays intact after pellet compression, the 100%-loaded SBA-15 should have a theoretical pellet density of $\sim 1.20 \text{ g cm}^{-3}$ (and 1.76 g cm^{-3} , assuming that the nanopore voids collapse; see details in the [Supporting Information](#)), whereas its actual density was 0.71 g cm^{-3} . This suggests that about 40% void space exists in the 100%-loaded SBA-15 sample. Assuming that the extra bulk NaCB₁₁H₁₂ in 133%-loaded SBA-15 fills some of these voids, the density is expected to increase to 0.80 g cm^{-3} , which compares well with the actual density of 0.79 g cm^{-3} for the 133%-loaded SBA-15 sample.

Strategies that can increase NaCB₁₁H₁₂ connectivity and reduce the fraction of void space should lead to significant improvements in nanocomposite conductivities. These might include using nanoporous silica with different morphologies, larger pore volume fractions, and more favorable compaction properties, as well as performing multiple infiltration/drying treatments with saturated salt solution to minimize intrapore voids.

It is worth noting that the observed nanoconfinement behavior for NaCB₁₁H₁₂ is somewhat different from that found for LiBH₄. In contrast to NaCB₁₁H₁₂, multiple studies of LiBH₄ nanoconfined in carbon, silica, and alumina scaffold

folds^{14,15,37–43} down to subambient temperatures indicate that only a fraction of the infiltrated material near the nanopore walls behaves in a nonbulk-like fashion, with highly reorientationally mobile BH₄[−] anions and highly diffusive Li⁺ cations, while the remaining fraction near the nanopore center displays more bulk-like behavior with much lower anion and cation mobilities. Moreover, unlike nanoconfined NaCB₁₁H₁₂, where no translational mobility of the otherwise rotationally liquid CB₁₁H₁₂[−] anions is observed by NMR, long-range diffusive motion of the BH₄[−] anions is indeed observed for the fraction of nanoconfined, nonbulk-like LiBH₄ residing near the nanopore wall,³⁸ suggesting the presence of a relatively more fluidic LiBH₄ interface layer and a possibly different conduction mechanism. It is thought that this highly conductive LiBH₄ layer results from compound-altering interactions with the nanopore wall and may involve the formation of an interfacial space-charge region.^{44–46}

In addition to the differences with nanoconfined LiBH₄, the intriguing results shown here for NaCB₁₁H₁₂@SiO₂ are also qualitatively dissimilar to the previously mentioned behavior for SiO₂-nanoconfined Li₂B₁₂H₁₂,^{17,18} where most, if not all, Li₂B₁₂H₁₂ was in a bulk-like ordered α -phase at ambient temperatures, with only a very minor fraction possibly in a highly conductive disordered β -phase normally only stable at much higher temperatures. Based on the known pore-size-dependent bifurcated phase behavior for nanoconfined LiBH₄ systems,^{40,41} it is reasonable to assume that Li₂B₁₂H₁₂ might also form a thin disordered-phase layer at the Li₂B₁₂H₁₂-SiO₂ interface with a predominant core of bulk-like Li₂B₁₂H₁₂, even if such bifurcation does not appear to be the case for NaCB₁₁H₁₂@SiO₂ for similar nanopore sizes. Nonetheless, whether or not the apparently unremarkable nanoconfined-Li₂B₁₂H₁₂ behavior is specific to particular (carba)borates and/or cations is a subject for further studies. Moreover, although the disordered NaCB₁₁H₁₂ polymorphs are superionic phases and are therefore clearly a major contributor to the favorable NaCB₁₁H₁₂@SiO₂ nanocomposite conductivities found in this study, at this time, we still do not know to what extent NaCB₁₁H₁₂@SiO₂ interface effects enable enhanced Na⁺ translational mobilities that may also be contributing.

CONCLUSIONS

Using a combination of techniques, we have shown that by depositing NaCB₁₁H₁₂ into nanoporous, high-surface-area silica via a simple aqueous salt infiltration method, it is possible to stabilize a bulk-like superionic phase down to cryogenic temperatures. This contrasts with bulk NaCB₁₁H₁₂, which can maintain its disordered superionic polymorphs only above $\sim 354 \text{ K}$. Even without any further optimization strategies, the nanocomposites presented here show a significantly higher cationic conductivity at room temperature ($3 \times 10^{-4} \text{ S cm}^{-1}$) than for bulk NaCB₁₁H₁₂ ($3 \times 10^{-6} \text{ S cm}^{-1}$) as well as for the best nanoconfined-LiBH₄-based composites in SiO₂ and Al₂O₃ ($\sim 1 \times 10^{-4} \text{ S cm}^{-1}$).^{14–16} The conductivity of NaCB₁₁H₁₂@SiO₂ can likely be further improved by a variety of factors, such as multiple solution loading/drying cycles and/or optimizing the choice of nanostructure used to stabilize the superionic phase. This could potentially solve two of the current issues: insufficient filling of salt in the nanocomposite, leading to less than full conductive connectivity, and the formation of excessive bulk NaCB₁₁H₁₂ coating the nanostructures and thus acting as a resistive layer at lower temperatures. We believe that fused

nanoporous SiO₂ macrostructures formed via sol–gel or similar synthesis processes to yield interconnecting porous channels, with no external nanoparticle surfaces, could ultimately prove to be better scaffold candidates. Finally, because ball-milling of NaCB₁₁H₁₂ and other polyhedral (carba)borate salts has been previously shown to promote the formation of high-temperature superionic disordered phases at ambient temperatures, a process that was further enhanced by ball-milling with other compounds,⁹ it may yet turn out to be worthwhile to ball-mill these types of salts together with either nanoporous or high-surface-area non-porous SiO₂ or Al₂O₃, as has already been done successfully with LiBH₄,^{15,45,46} instead of the current solution infiltration procedure. If intermixed finely enough and in the right proportions, the resulting compressed composites could have fully connective three-dimensional networks of superionic salt nanoconfined and stabilized among the oxide scaffold particles, with reduced void volume and thus improved overall conductivity.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.1c03589>.

Complementary DSC, PXRD, NVS, NMR, QENS, and impedance data (PDF)

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Notes

The authors declare no competing financial interest.

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