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Supplementary Information

A highly stable sodium solid-state electrolyte based on a dodeca/deca-borate equimolar mixture

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Experimental Details

Synthesis: $Na_2B_{12}H_{12}$ (anhydrous) and $Na_2B_{10}H_{10}$ were purchased from Katchem. $Na_2B_{12}H_{12}$ was used and characterized as received and $Na_2B_{10}H_{10}$ was first dried under vacuum for 6 h at 160 °C. $Na_2(B_{12}H_{12})_{1-x}(B_{10}H_{10})_x$ samples with composition x=0.1 to 0.6 were prepared by mixing the appropriate amounts of precursors using mechanical ball-milling. Samples were ball-milled in a Spex 8000M shaker mill with 5 mm balls and a balls-to-sample mass ratio of 10 to 1 for three times 15 min with 5 min breaks to avoid overheating (sample referred to as “before heat treatment”). After ball-milling, a heat treatment was carried out under vacuum ($p < 10^{-3}$ mbar) at 270 °C for 12 h to fully react and crystalize the compounds (sample referred to as “after heat treatment”). Samples were handled in an argon-filled glove-box to avoid exposure to moisture.

Differential Scanning Calorimetry (DSC): Measurements were conducted on a Netzsch STA449 F3 Jupiter. The samples were cycled three times at heating and cooling rates of 10 K min^{-1} between -100 °C and 300 °C. The samples (~10 mg) were handled in sealed Al crucibles and the measurements were carried out under He flow.

Powder X-ray Diffraction (XRD): XRD patterns were collected on a Bruker D8 diffractometer equipped with a Göebel mirror selecting CuK_{α} radiaton (λ=1.5418 Å). Samples were sealed into quartz capillaries, filled under argon atmosphere. High temperature measurements were performed using an MRI high temperature capillary furnace.
The refinements were performed using the Maud refinement software (*L. Lutterotti, S. Matthies, H.-R. Wenk, A.J. Schultz and J. Richardson, J. Appl. Phys., 81[2], 594-600, 1997*). The background was interpolated from manually chosen points. As there is no structural model for $Na_2(B_{12}H_{12})_{0.5}(B_{10}H_{10})_{0.5}$, we used the structural model of $Na_2B_{10}H_{10}$ (Udovic et al.[17]) to refine the lattice parameters only.
Structure visualizations were obtained in VESTA (*K. Momma and F. Izumi, J. Appl. Crystallogr., 44, 1272-1276, 2011*)

NMR spectroscopy: Solid-state magic angle spinning (MAS) NMR measurements experiments were performed on a Bruker Avance-400 NMR spectrometer using a 4 mm CP-MAS probe. The ^{1}H, ^{11}B and ^{23}Na NMR spectra were recorded at 13 kHz MAS rates as single pulse experiments using pulse lengths $< \pi/6$ applying SPINAL-64 proton decoupling in the case of boron (no influence observed on line width for ^{23}Na NMR spectra with or without decoupling of ^{1}H). Sufficiently long relaxation delays for full recovery of signal intensities were applied.

Infrared spectroscopy: IR spectra were acquired on a temperature controlled Specac ATR setup mounted on a Biorad Excalibur FT-IR instrument and measured between 600 and 4000 cm^{-1} with a resolution of 1 cm^{-1}.

AC and DC measurements: The powder samples were pressed into pellets of 12mm in diameter and a thickness between 1 and 2 mm with a pressure of 0.9 GPa, loaded in air tight stainless steel cells and contacted between two spring loaded electrodes. Indium foils were mechanically pressed on the pellets surface to improve the contact between the sample and the molybdenum electrodes, for impedance spectroscopy measurements.
Ionic conductivity was measured by electrochemical impedance spectroscopy using a BioLogic VMP3 **multi-channel potentiostat** in a frequency range from 1 MHz to 1 Hz with a voltage amplitude of 50 mV. Temperature-dependent measurements were performed by placing the cell in a climatic chamber and equilibrating the cell for 2 h at each temperature. The pellet resistance R was extracted from the last measurement at each temperature, at the intercept with the x-axis of fitted semi-circles and/or linear spikes in the Nyquist plots. Na^+ conductivity is then $\sigma = \frac{1}{R} * \frac{l}{A}$ where A and l are the area and thickness of the pellet, respectively
Cyclic voltammetry and galvanostatic cycling were conducted using the same BioLogic VMP3 multi-channel potentiostat. Assessment of the oxidative stability was done using a special low-current channel for the VMP3 with a current resolution of 80 fA.

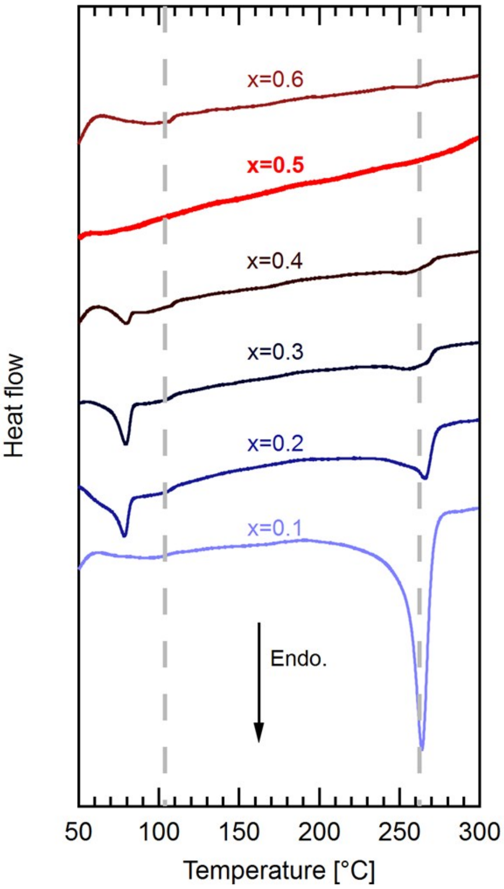

Fig. S1. Differential scanning calorimetry heating curves of $Na_2(B_{12}H_{12})_{1-x}(B_{10}H_{10})_x$ with $0.1 \le x \le 0.6$. Samples were cycled three times between 30 and 300 °C with a heating rate of 10 K min^{-1}. Data for the last (3rd) heating cycle are shown. The grey dashed lines indicate the onset temperature of the transitions of $Na_2B_{10}H_{10}$ (100 °C) and $Na_2B_{12}H_{12}$ (260 °C).

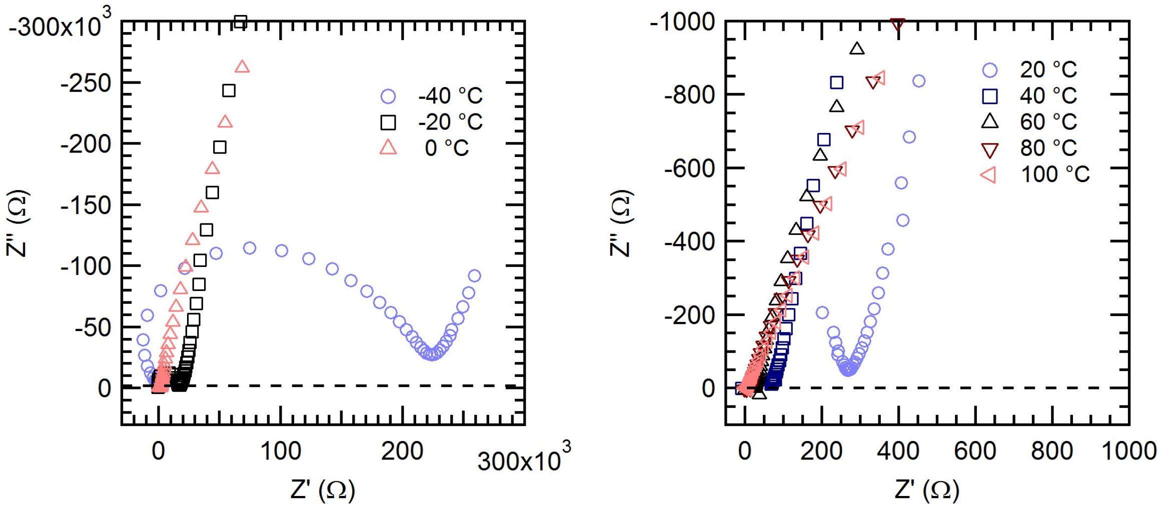

Fig S2. Exemplary Nyquist plots of impedance data measured in Mo|In|$Na_2(B_{12}H_{12})_{0.5}(B_{10}H_{10})_{0.5}$|In|Mo 2-electrode configuration upon the cooling cycle.

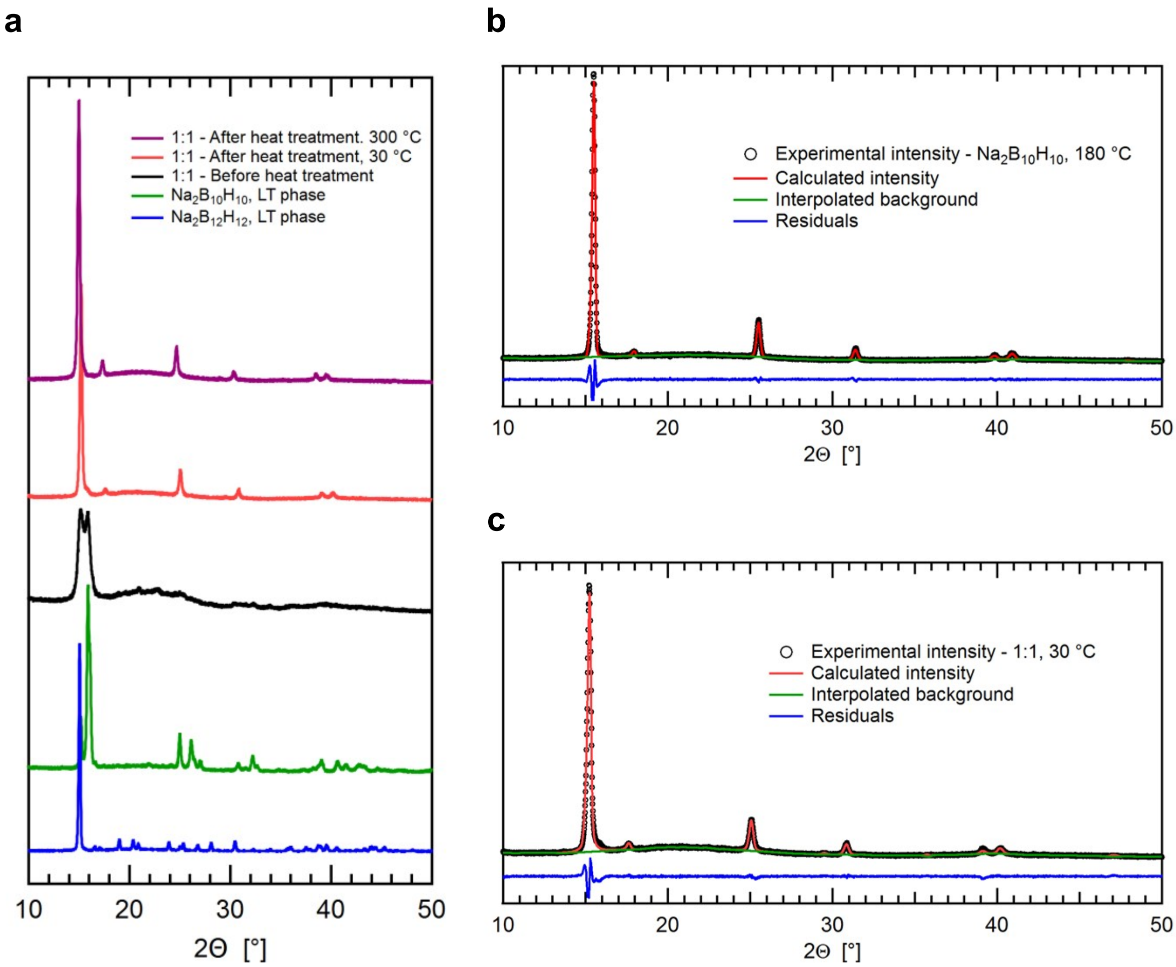

Fig S3. (a) XRD patterns at 30 °C of $Na_2B_{12}H_{12}$, $Na_2B_{10}H_{10}$, and $Na_2(B_{12}H_{12})_{0.5}(B_{10}H_{10})_{0.5}$ before and after heat treatment, and of $Na_2(B_{12}H_{12})_{0.5}(B_{10}H_{10})_{0.5}$ after heat treatment (12h, 270 °C), measured at 300 °C. **(b & c)** Refinement results of $Na_2B_{10}H_{10}$ and $Na_2(B_{12}H_{12})_{0.5}(B_{10}H_{10})_{0.5}$

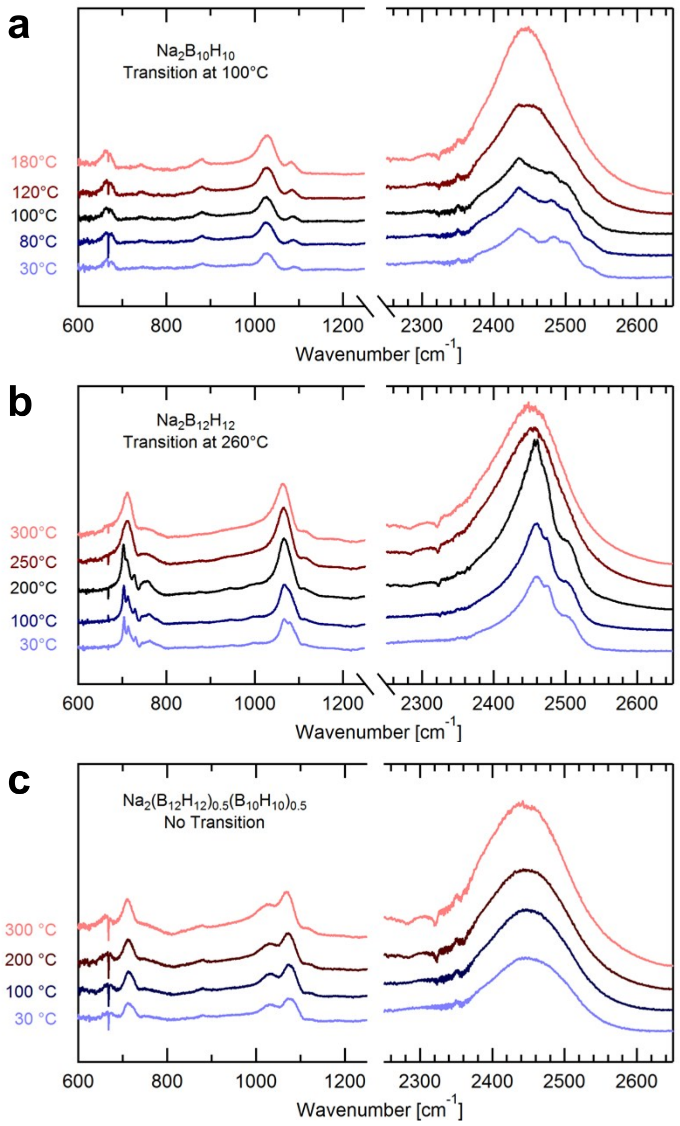

Fig S4. Temperature-dependent IR spectra of (a) $Na_2B_{10}H_{10}$, (b) $Na_2B_{12}H_{12}$, and (c) $Na_2(B_{12}H_{12})_{0.5}(B_{10}H_{10})_{0.5}$.

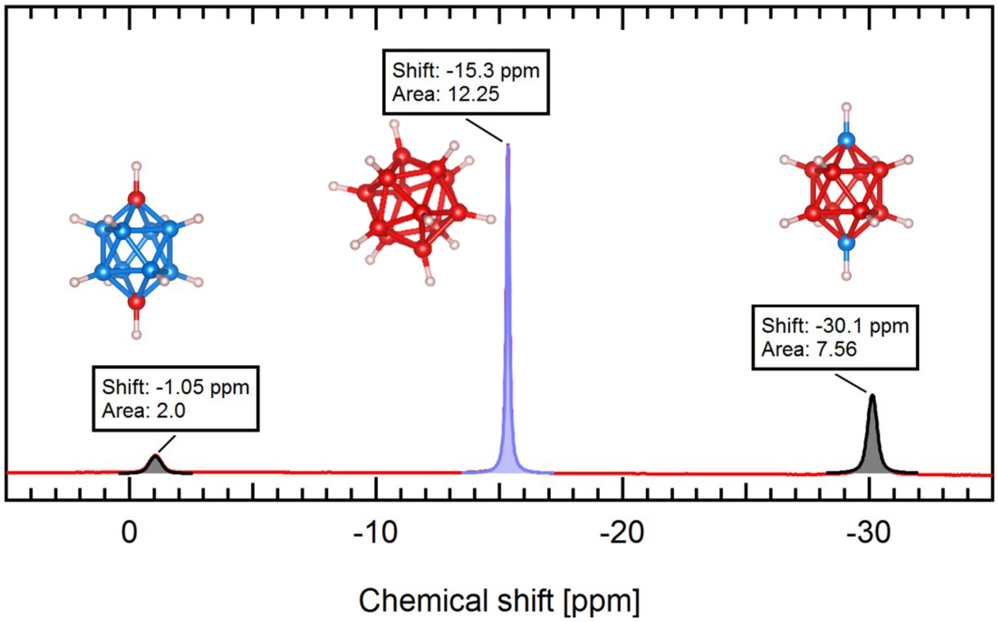

Fig S5. Room temperature ^{11}B liquid-state NMR spectrum of $Na_2(B_{12}H_{12})_{0.5}(B_{10}H_{10})_{0.5}$ fully dissolved in D_2O showing the quantification of the boron species in the borate anions. The peak areas were determined from fitting of the resonances using Lorentzian shapes.