

Supporting Information: Mixed Anion *Closo*-Carbaboborates as Na-Superionic Conductors

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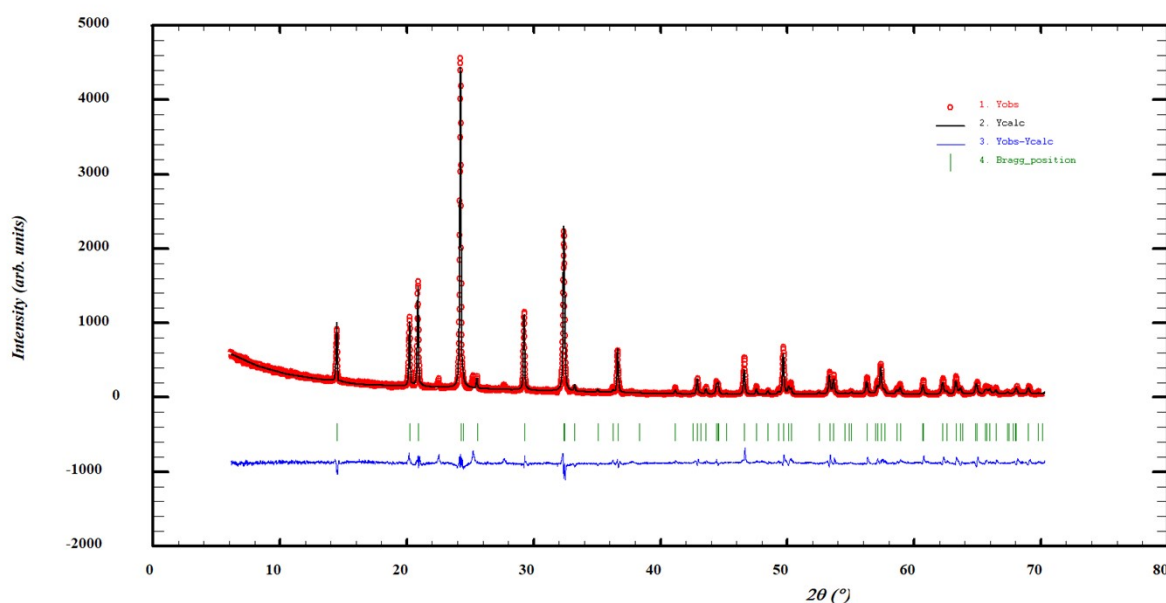


Figure S1. Rietveld refinement of $\text{NaTi}_2(\text{PO}_4)_3$ measured at room temperature, $\lambda = 1.54056 \text{ \AA}$, showing the experimental (red circles), calculated (black line) PXD patterns as well as the difference plot (blue line). The red tick marks show the Bragg positions of $\text{NaTi}_2(\text{PO}_4)_3$. Discrepancy factors: $R_p = 11.5 \%$, $R_{wp} = 9.22 \%$ (not corrected for background), $R_p = 24.7 \%$, $R_{wp} = 10.5 \%$ (conventional Rietveld R-factors).

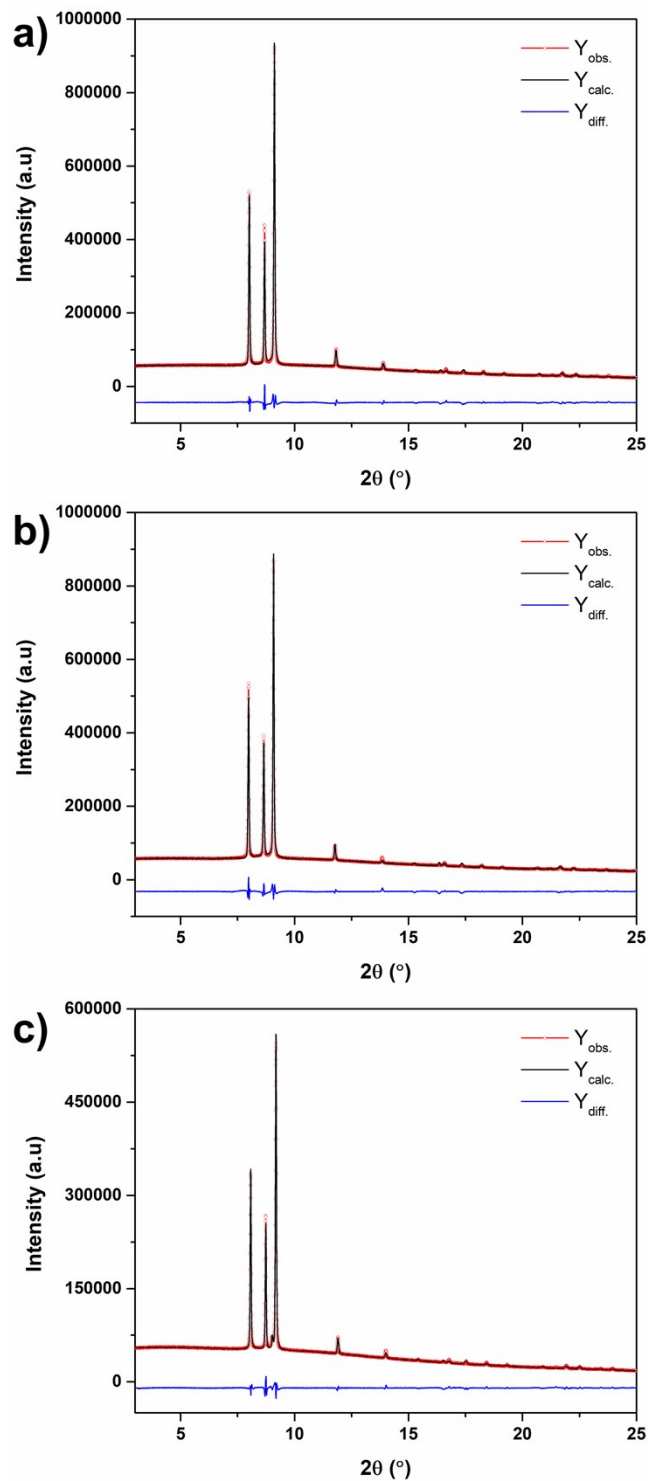


Figure S2. Rietveld refinement plots of s3 (a), s4 (b) and s5 (c) using the revised structural model of *ht*-NaCB₉H₁₀ with an adjusted B- and H-occupancy according to the composition determined from ¹¹B NMR. The SR PXD data is measured at $T = -23$ °C using $\lambda = 0.825850$ Å, showing experimental (red circles) and calculated (black line) PXD patterns, and a difference plot below (blue line).

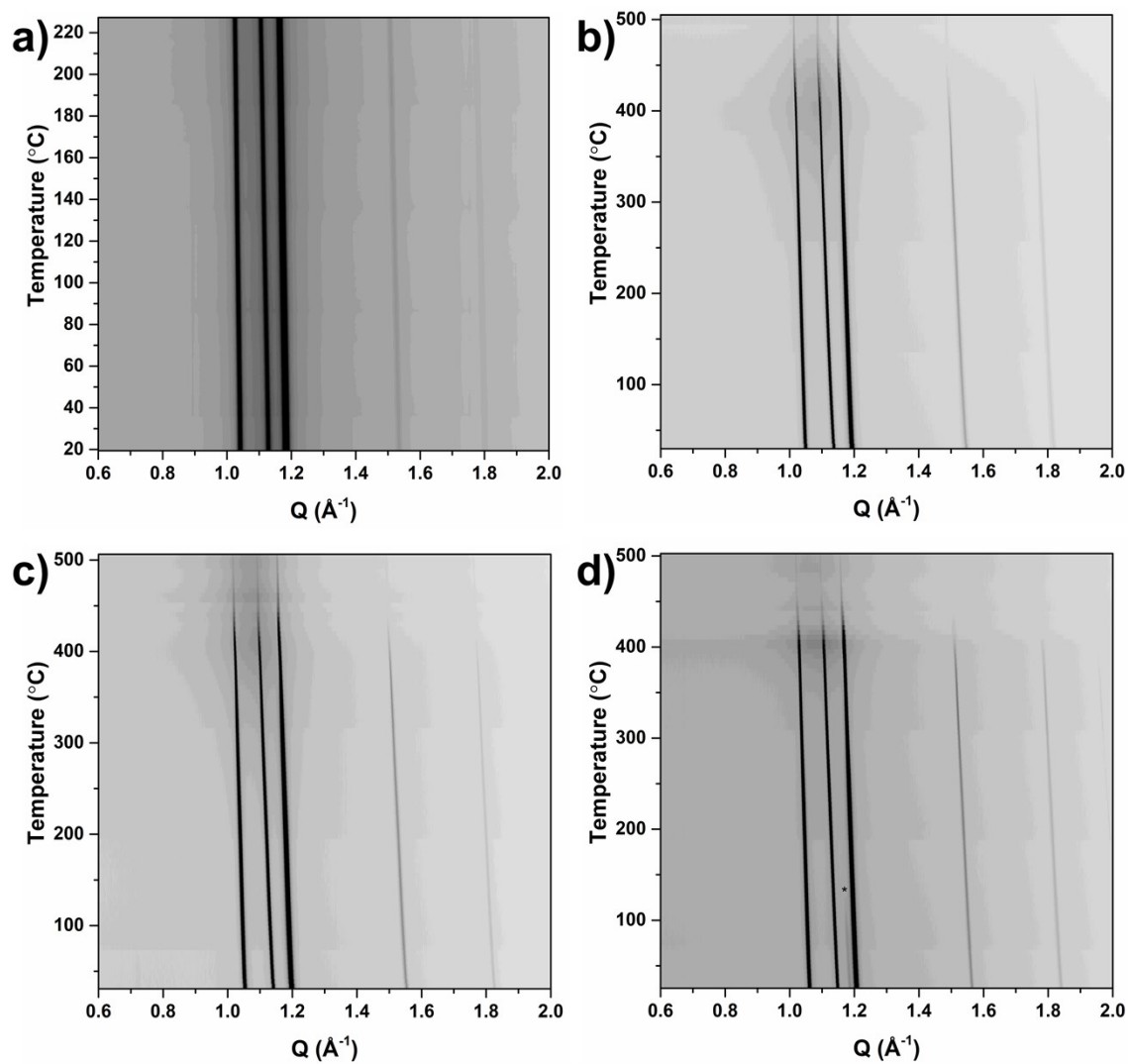


Figure S3. *In situ* synchrotron radiation powder X-ray diffraction data of **s2** (a), **s3** (b), **s4** (c) and **s5** (d). The data has been collected at DanMAX (**s2**) and I11 (**s3-s5**) with a heating rate of 5 °C/min.

Table S1. Linear thermal expansion of the unit cell volume, α_v , for the *P31c* phase in **s1-s5** and *ht*-NaCB₉H₁₀.

Sample	Temperature range (°C)	Expansion coefficient ($\times 10^{-5} \text{ K}^{-1}$)
s1	0-225	27
s2	25-225	29
s3	25-500	27
s4	25-500	27
s5	25-500	29
NaCB₉H₁₀	0-225	29

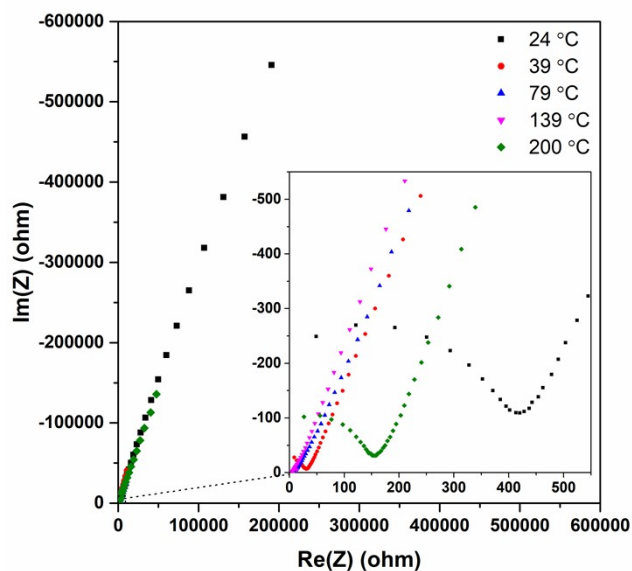


Figure S4. Nyquist plots of **s1** during heating.

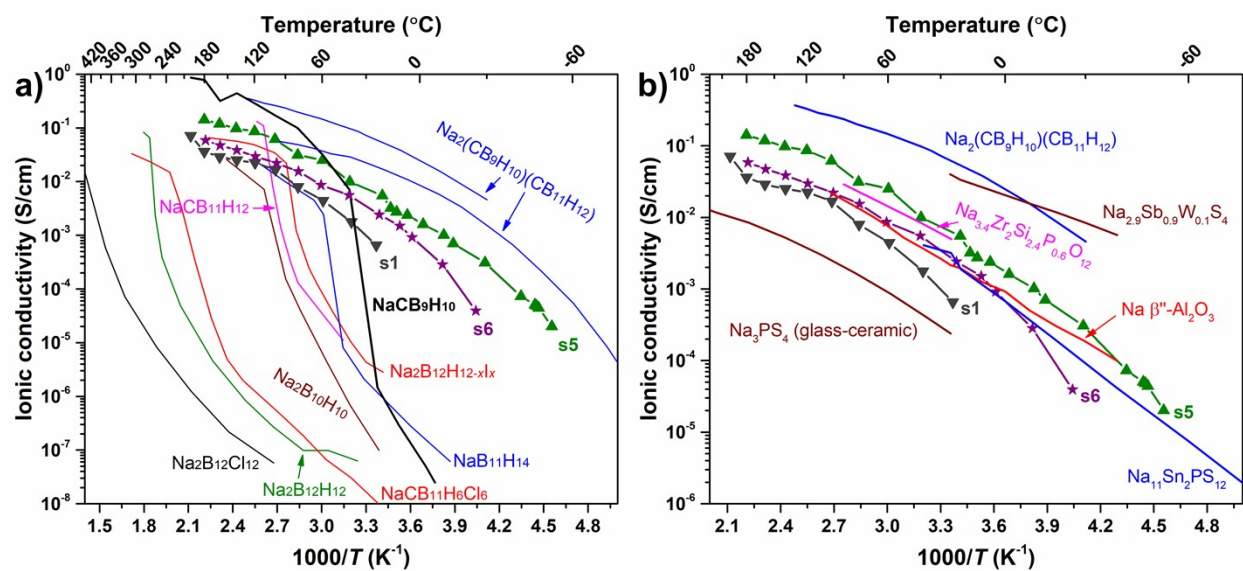


Figure S5. Temperature-dependent ionic conductivity of **s1**, **s5** and **s6** compared to other sodium *closo*-borates (a) and other state-of-the-art sodium ionic conductors (b).^{1–14}

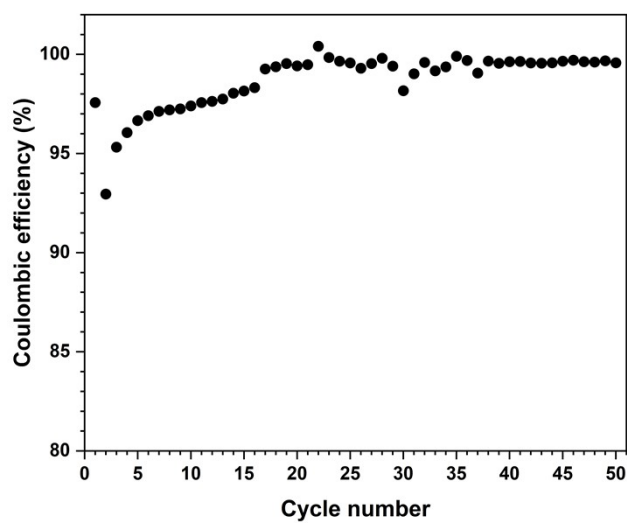


Figure S6. Coulombic efficiency of the galvanostatic cycling of a Na|s6|NaTi₂(PO₄)₃ cell (Fig. 5d) at a C/10 rate (10 hours per 2 Na⁺) between 1.5 V and 2.5 V at room temperature. The applied stack pressure was ~7.7 MPa.

Supporting references

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