Supporting information for:

"Sodium Superionic Conduction in $Na_2B_{12}H_{12}$"

Terrence J. Udovic,[a] Motoaki Matsuo,[b] Atsushi Unemoto,[c] Nina Verdal,[a,d] Vitalie Stavila,[e] Alexander V. Skripov,[f] John J. Rush,[a,d] Hitoshi Takamura,[g] and Shin-ichi Orimo[b,c]

[a] NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-6102, USA

[b] Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

[c] WPI-Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

[d] Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2115, USA

[e] Sandia National Laboratories, Livermore, CA 94551, USA

[f] Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences, Ekaterinburg 620990, Russia

[g] Graduate School of Engineering, Tohoku University, Sendai, 980-8579, Japan

Synthesis of $Na_2B_{12}H_{12}$:

The compound was prepared from $Cs_2B_{12}H_{12}$ via an ion-exchange method, as in: Her *et al.*, *J. Phys. Chem. C*, 2009, **113**, 11187. In a typical synthesis, around 2 g $Cs_2B_{12}H_{12}$ was dissolved upon heating in 80 mL H_2O and the warm solution was passed through an Amberlite[1] IR-120 ion-exchange column in H^+ form. The acidic fraction, aqueous $(H_3O)_2B_{12}H_{12}$, was collected and neutralized with 0.1 M aqueous NaOH at room temperature until reaching a pH of 7. The solvent was removed using a rotary evaporator at 323 K and the resulting solid was dried for around 4 h in vacuum at 623 K. The room-temperature, monoclinic, anhydrous $Na_2B_{12}H_{12}$ structure was verified by x-ray powder diffraction.

[1] The mention of all commercial suppliers in this paper is for clarity. This does not imply the recommendation or endorsement of these suppliers by NIST.

Experimental Procedures:

The ionic conductivities were determined in heating and cooling runs repeatedly in the temperature range between 303 K and 573 K by the AC complex impedance method using an NF FRA5097 frequency response analyzer over a frequency range of 10 Hz to 10 MHz. All measurements were performed under Ar. The powder sample was pressing into a pellet ≈8 mm in diameter and ≈3 mm in thickness without sintering. This corresponded to a pellet density of ≈1.13g/cc, which is close to the bulk density of $Na_2B_{12}H_{12}$. Au foils were used as electrodes and were mechanically fixed on both faces of the pelletized sample. The resistances of the sample were obtained by least square fittings of a single arc in the high-frequency range using equivalent circuits of a parallel combination of a resistance and a capacitance. At high temperature, since only a spike caused by the electrode contribution was observed, the resistance values were calculated from the intercept of the spike.

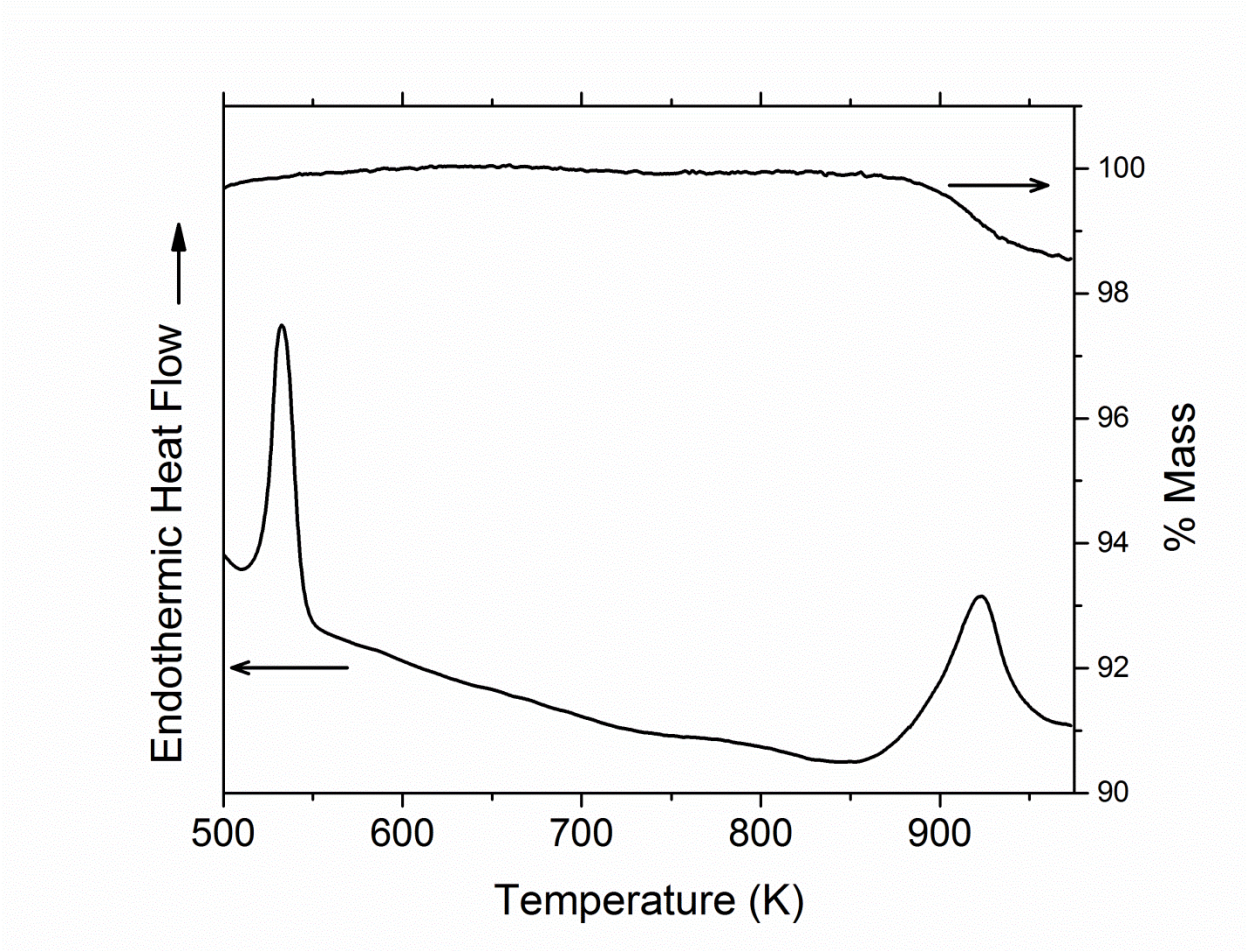

Figure S1. The DSC (left axis) and TGA (right axis) measurement of $Na_2B_{12}H_{12}$ show the phase transition at 529 K (upon heating from room temperature, 5 K/min). The endothermic peak above 860 K signals decomposition and is accompanied by a 1.1 % mass loss. $Na_2B_{12}H_{12}$ is stable below this temperature.