



	Experiment title: Pressure induced phase transitions in solid state ionic conductors	Experiment number: 01-02-1144
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Report:

All-solid-state batteries employing solid-state electrolytes promise higher energy and power densities, wider working temperature windows and increased safety as compared to state-of-the-art lithium ion batteries using flammable organic liquid electrolytes. Metal borane compounds, *i.e.* ionic compounds containing $[B_{10}H_{10}]^{2-}$ or $[B_{12}H_{12}]^{2-}$ anions, exhibit high ionic conductivities (of up to 0.1 S/cm at elevated temperature), wide electrochemical stability windows, high thermal stabilities and low toxicity. Due to these favourable properties, they are discussed as solid-state electrolytes for a new generation of metal ion batteries.

The discovery of ionic conductivity of the order 0.1 S/cm above the phase transition at 540 K in $Na_2B_{12}H_{12}$ [1] has triggered extensive research towards the understanding and improvement of ion mobility in dodecaboranes. The effect of high Na conductivity is related to a polymorphic transition from a monoclinic (*fcc* based) to a cubic phase with *bcc* arrangement of $[B_{12}H_{12}]^{2-}$ anions [2]. However, the exact relation between ion mobility and the structure remains unclear. For the large class of metal oxides and sulfides, a structure-related model of the conductivity was proposed [3]. It indicates that *bcc* anion arrangement is preferable to reach high lithium ionic conductivity. A comparable model does not yet exist for metal borane compounds. We have performed DFT calculations under external pressure that indicate that in compounds with large dodecaborane anions, high ionic mobility can also be expected for *hcp* anion arrangement, due to the large size difference between cations and anions [4].

In order to study the relation between pressure and structure type, and to develop a model for the structure relation of the ionic conductivity, we conducted high pressure studies for $M_2B_{12}H_{12}$ with $M = Li, Na, K$, and mixed $Na_2B_{12}H_{12}/Na_2B_{10}H_{10}$ systems, combining SR-PXD and Raman spectroscopy.

The pure samples were purchased from Katchem and used as received, the mixed $Na_2B_{12}H_{12}/Na_2B_{10}H_{10}$ sample was prepared as described earlier [5]. The pressure dependent measurements were carried out at room temperature, using diamond anvil cells (DAC), the use of a pressure-transmitting medium was not necessary to achieve quasi hydrostatic conditions. The samples were loaded together with ruby crystals for pressure calibration. The pressure was determined by optical spectroscopy prior and after the diffraction measurement to guarantee stable conditions. *In situ* Raman spectroscopy was used to complement the diffraction data. The

X-ray data were recorded using a Pilatus detector placed at a distance of 411 mm from the sample and an X-ray wavelength of 0.71414 Å was used. The 2D diffraction patterns were integrated using the Bubble software. The sample-detector geometry was calibrated with a LaB₆ NIST standard. All sample handling was carried out in inert atmosphere.

We found that Na₂B₁₂H₁₂ (phase I, *P2₁/c*) undergoes two phase transitions under pressure, the first one at 0.5 GPa (phase II, *Pbca*) and the second between 5.4 and 8.1 GPa (phase III, unknown). The transition phase II → phase III is fully reversible. The transition phase I → phase II seems to be irreversible, indicating that the stability of both phases at ambient pressure is similar, therefore the kinetics is too slow to allow the transition back to be observed within the present experiment.

The crystal structure of phase II was solved using the *ab-initio* method with parallel tempering algorithm implemented in FOX [6] and then refined with Rietveld method with the JANA2006 software [7]. After refinement the following agreement factors were obtained, Rp = 10.9 %, Rwp = 14.2 % (conventional) and GOF = 4.87. Figure 1 shows the crystal structure of phase II, the anions B₁₂H₁₂²⁻ are packed in a fcc fashion as for the HT crystal phase of Li₂B₁₂H₁₂ [2], Na₂B₁₀H₁₀ [8] and Na₂(B₁₀H₁₀)_{0.5}(B₁₂H₁₂)_{0.5} [5] which are ionic conductive phase. Sodium occupies the tetrahedra sites 8c but are slightly shifted off the gravity center (¼, ¼, ¼) of the tetrahedral site.

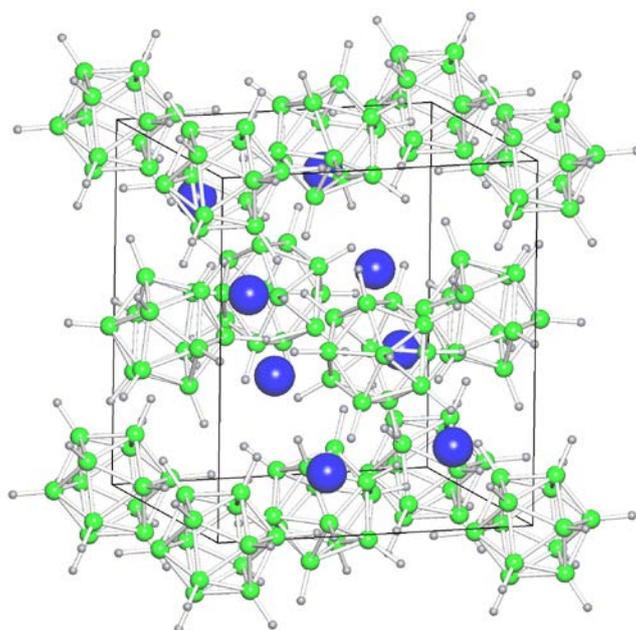


Fig. 1: Crystal structure of phase II at 0.2 GPa.

Based on this work one manuscript is in preparation:

Data treatment of the other investigated compounds is still ongoing.

Acknowledgements

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