Experimental report

12/09/2018

Proposal: **7-03-172** **Council:** 4/2018

Title: Anion Reorientations in Na2B12H12 at Elevated Pressure

Research area: Materials

This proposal is a new proposal

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Experimental team: Tatsiana BURANKOVA
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Local contacts: Bernhard FRICK

Samples: Na2B12H12

Instrument	Requested days	Allocated days	From	To
IN16B	6	3	04/09/2018	07/09/2018

Abstract:

Under elevated pressure the structure of the solid-ionic conductor Na2B12H12 can be manipulated providing a new dimension for the rational design of such materials with better conductivity. Our group has recently characterised a high pressure phase of Na2B12H12, which can be stabilised at ambient pressure and adopts a fcc-like structure favourable for higher conductivity and faster dynamics. Here we propose to study reorientational anion motions in Na2B12H12 undergoing the pressure-induced phase transition. The aim of our study is to elucidate the connection between the anion supported conduction mechanism, anion reorientational mobility and crystal structure of this solid-state electrolyte.

Anion Reorientations in $Na_2B_{12}H_{12}$ at Elevated Pressure

Proposal No.: 7-03-172

Experimental team: T. Burankova, R. Moury, H. Hagemann, Jan P. Embs, A. Remhof.
Instrument: IN16B (04.09.2018–07.09.2018)
Local contact: Bernhard Frick

The sample used in the present study is $Na_2B_{12}H_{12}$ (phase I, $P2_1/c$) 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 between phase II and phase III is fully reversible. The transition phase I → phase II seems to be irreversible. Moreover, the high pressure phase II (Fig. 1) can be stabilized at ambient pressure and adopts a fcc-like structure, which was found to be a kind of packing favorable for higher conductivity and faster dynamics.

A high-pressure gas cell made of CuBe alloy (04PG70CB6) was used to perform both elastic and inelastic fixed window scans (EFWS/IFWS, Figure 1) on $Na_2B_{12}H_{12}$ in the temperature range of 300–530 K on heating and cooling at pressure values of p_1 = 120 bar, p_2 = 5.0 kbar, and p_3 = 150 bar. To avoid the strong neutron absorption by the ^{10}B isotope present in natural B, the sample with isotopically enriched ^{11}B was purchased from Katchem. The elastic signal of the empty container was equal to approximately one half of the sample signal due to the strong neutron absorption of the cell material. To perform a sophisticated background subtraction and multiple scattering corrections, McStas simulations will be employed.

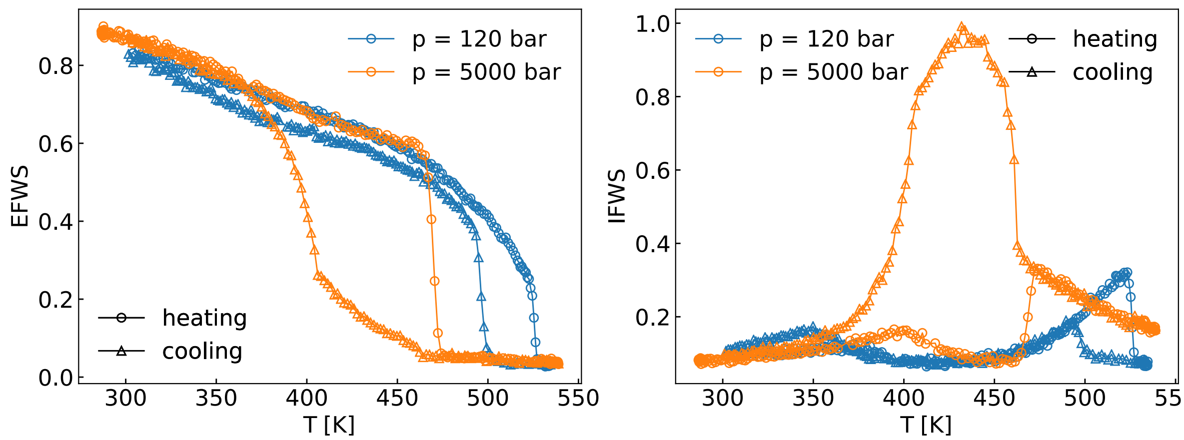

Figure 1. EFWS (left panel) and IWFS (right panel) measured on cooling and heating at the low (p_1 = 120 bar) and elevated pressure values (p_2 = 5.0 kbar).

The preliminary analysis of the EFWS/IFWS at 120 bar showed the presence of two localized processes. The first one appears in the temperature range 300–400 K on heating and is consistent with the mechanism of incomplete reorientations by a small angle. The onset of the second process appears at temperatures above 450 K and corresponds to presumably uniaxial rotation of the $B_{12}H_{12}$ anions. The transformation to the high temperature (HT) phase leads to significant enhancement of anion dynamics above 520 K. At the elevated pressure of 5 kbar, the first bump corresponding to small angle anion reorientations is shifted to higher temperatures, which corresponds to slower relaxation times on average. The slower anion motion is observed for the HT phase at high pressure as well. However, the cooling cycle exhibits at least two phase transitions, the one between 400 and 460 K displaying unprecedented fast anion reorientations. The heat treatment of the sample at high pressure results to the reversible transition to phase I on releasing the pressure to 150 bar.