ELECTRONIC SUPPLEMENTARY INFORMATION

"Synthesis of amorphic and hexagonal boron nitride via high temperature treatment of NH_3BH_3 and $Li(BH_3NH_2BH_2NH_2BH_3)$"

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Contents:

1. Synthesis of $Li(BH_3NH_2BH_2NH_2BH_3)$ and pyrolysis procedure

Labmaster MBraun and Vigor gloveboxes filed with argon 5.0 (O_2 < 1 ppm; H_2O < 1 ppm) were used to store chemicals and perform sample manipulations including syntheses and reactors sealing and opening. Fine quality anhydrous reagents were used: NH_3BH_3 (98%, JSC Aviabor), LiH (95%, Sigma Aldrich) and h-BN (99.5%, max 10 µm, Sigma Aldrich).

NH_3BH_3 and h-BN were used as purchased. Li[B3N2] was synthesised mechanochemically in a direct reaction of NH_3BH_3 and LiH with further thermal treatment at 75°C according to the following equation [*Phys. Chem. Chem. Phys.* 16 (2014) 23340–23346; *Dalton Trans*. 52 (2023) 3586–3595]:

$$LiH + 3NH_3BH_3 \rightarrow Li(BH_3NH_2BH_2NH_2BH_3) + 2H_2\uparrow + NH_3\uparrow$$

Furnace pyrolysis was performed in Neoterm NT 1313 KXP 3 ceramic furnace, operating up to 1000°C, using customised reactors made of monel (70% Ni, 30% Cu) or 4H13 chromium steel, sealed under argon using copper gaskets. The samples were annealed at target temperatures for 1 h and then left to cool down in sealed reactors inside the furnace.

Hot isostatic pressing (HIP) was performed in EPSI HIP 300-125/200 GM operating to 1000 bar and 1000°C with argon N 5.0 atmosphere using steel capsule reactors. The samples were annealed at target temperature and pressure for 30 minutes and then left to cool down inside the apparatus.

First, the powder samples were encapsulated in steel capsules under argon and then heated to 300°C under vacuum. In the next stage, the capsules containing the samples were placed in the HIP chamber and subjected to 1 mbar vacuum to remove air. In the next stage, argon was inserted into the system to reach the pressure of several bars. Once the softening temperature of the capsule reached 800°C, the argon pressure in the HIP chamber was increased *via* an external compressor. Once the preset pressure was achieved, the sample was held for the set period of time (30 minutes) at the preset conditions (1000°C / 1000 bar). After accomplishing the HIP treatment, the system was cooled down to 300°C. Then, the system was decompressed to atmospheric pressure and further cooled down to room temperature.

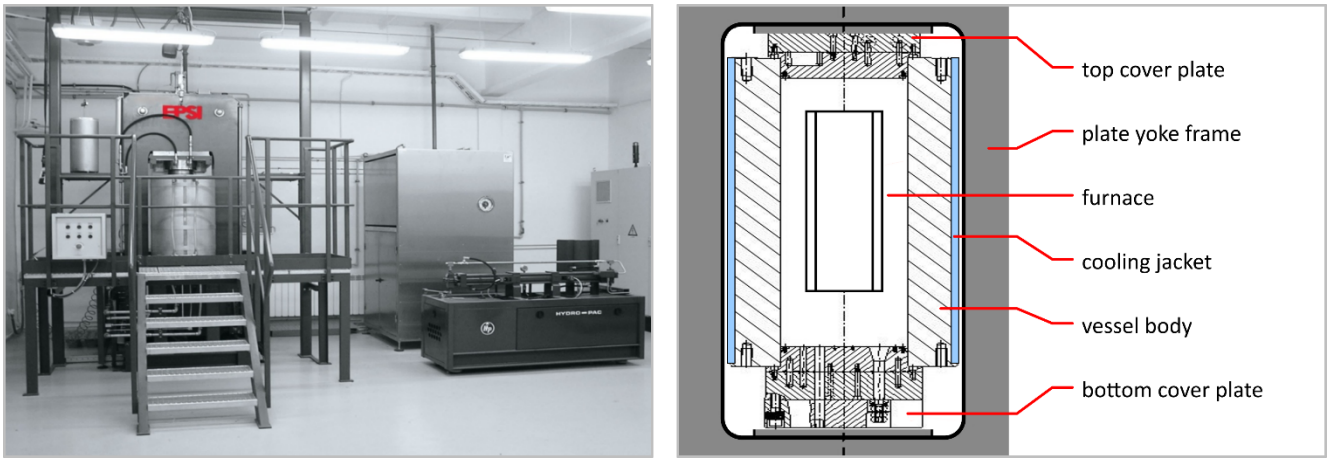

Fig. S1. General view of the HIP apparatus at Łukasiewicz-ICIMB (left) and a scheme of the HIP chamber (right).

2. Comparison of IR absorption spectra and PXRD patterns of the products of pyrolysis of NH_3BH_3

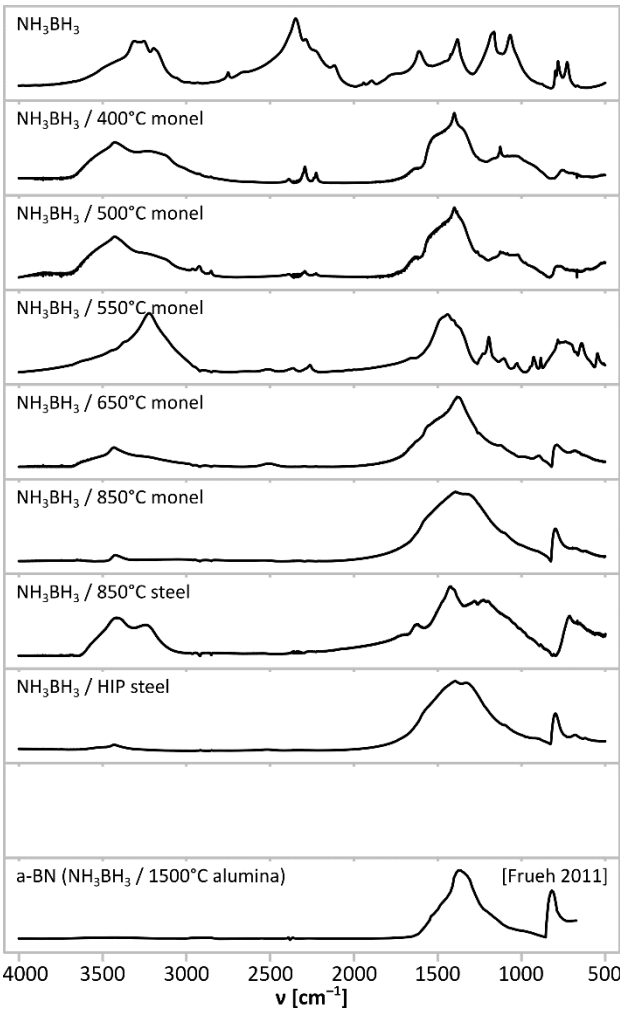

Fig. S2.1. Comparison of IR absorption spectra of neat ammonia borane and the materials decomposed in monel reactors (400°C, 500°C, 550°C, 650°C, 850°C), steel reactors (850°C) and HIP (1000°C/1000 bar). For comparison the spectrum of a-BN obtained by Frueh et al., *Inorganic chemistry* 50 (2011) 783–792 (digitalised).

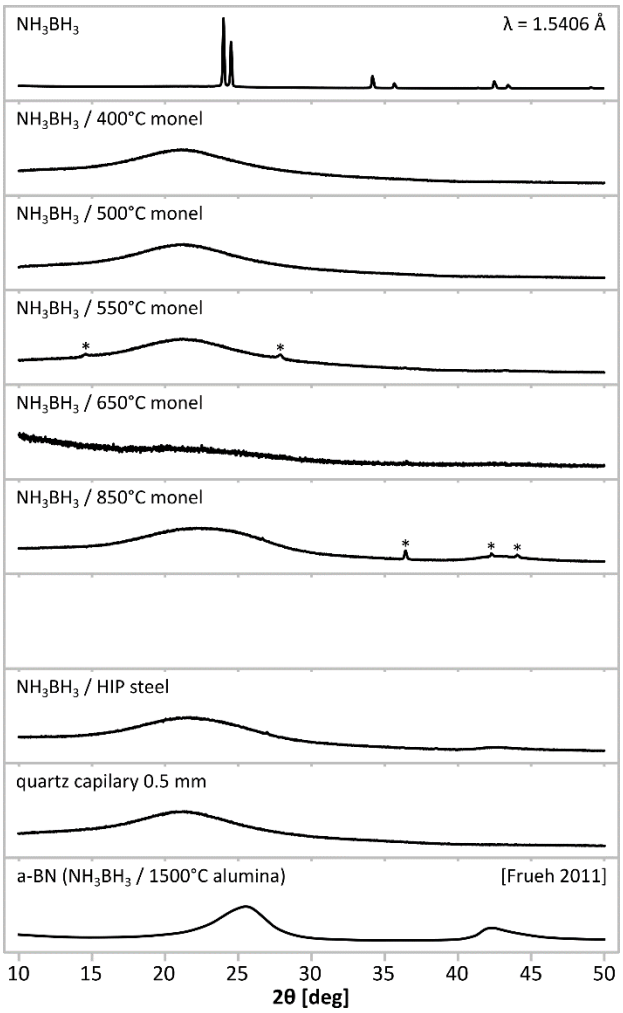

Fig. S2.2. Comparison of X-ray powder patterns of neat ammonia borane and the materials decomposed in monel reactors (400°C, 500°C, 550°C, 650°C, 850°C), and in HIP (1000°C/1000 bar). For comparison the pattern of empty 0.5 mm quartz capillary spectrum of a pattern of a-BN obtained by Frueh et al., *Inorganic chemistry* 50 (2011) 783–792 (digitalised with omission of sample holder signals). * unknown phases.

3. SEM images of the products of pyrolysis of NH_3BH_3

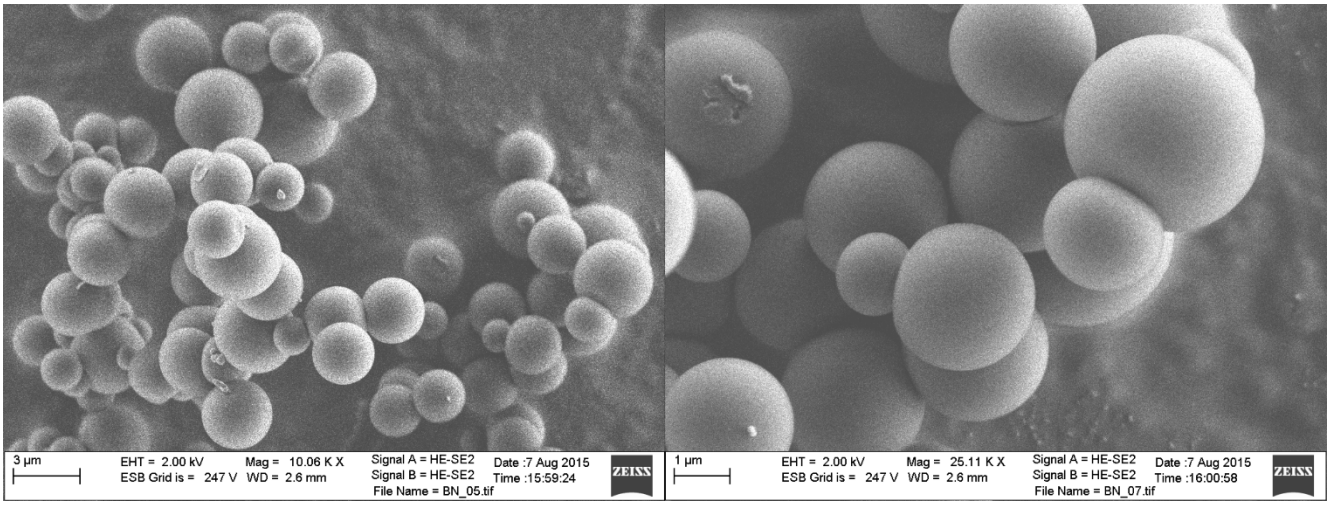

Fig. S3.1. SEM images of the product of pyrolysis of ammonia borane at 850°C in a monel reactor.

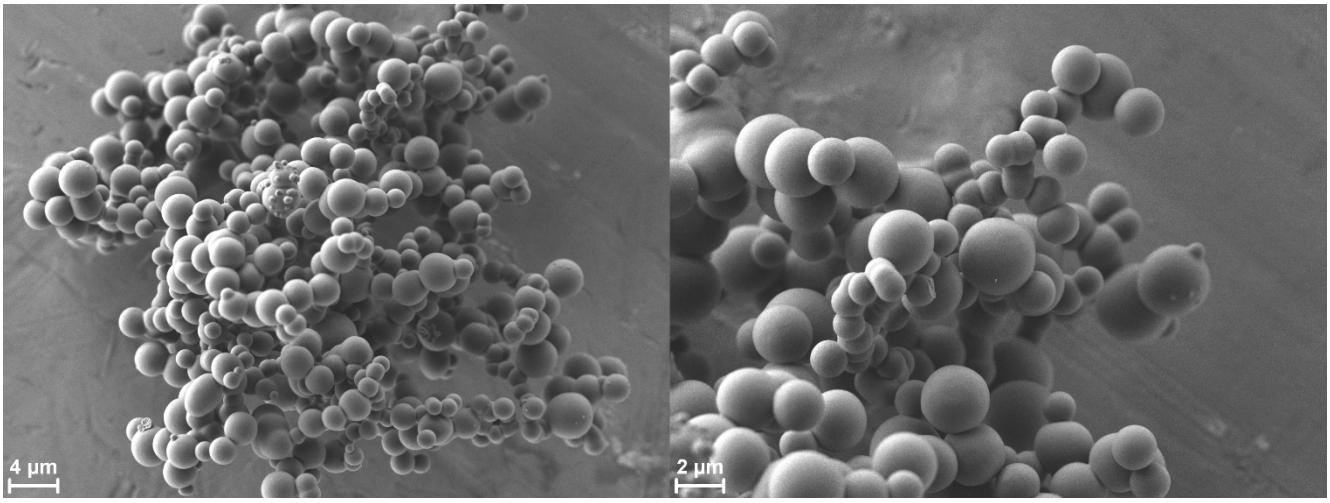

Fig. S3.2. SEM images of the product of pyrolysis of ammonia borane at 1000°C under 1000 bar (HIP) in a steel capsule.

4. SEM images of the products of pyrolysis of $Li(BH_3NH_2BH_2NH_2BH_3)$

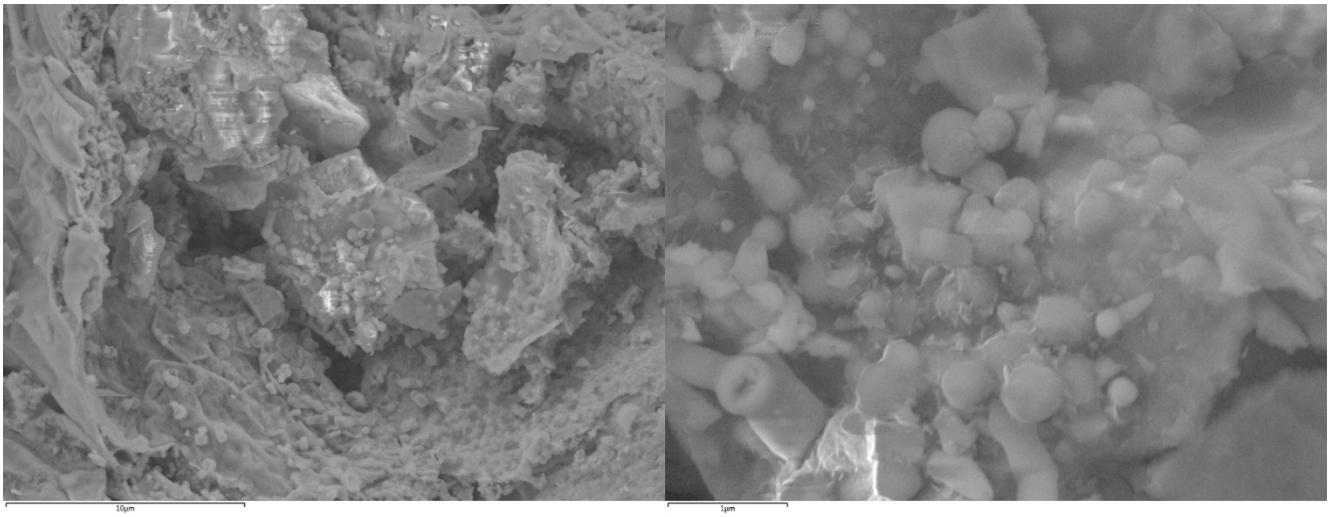

Fig. S4.1. SEM images of the product of pyrolysis of $Li(BH_3NH_2BH_2NH_2BH_3)$ at 850°C in a monel reactor.

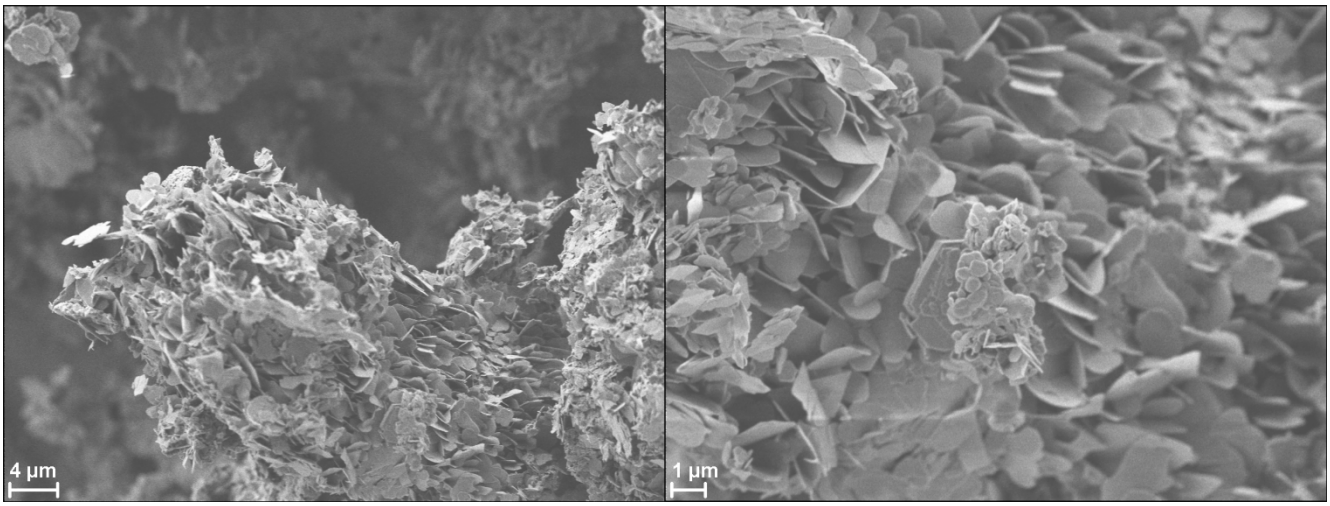

Fig. S4.2. SEM images of the product of pyrolysis of $Li(BH_3NH_2BH_2NH_2BH_3)$ at 1000°C under 1000 bar (HIP) in a steel capsule