

Report form of Joint Research Project at ZAIKEN (2018)

Title of Project	Design of sp^2 and sp^3-boron nitride with tuned crystallinity via precursor chemistry		
Priority Area	Development of material engineering to reduce loads on the environment		
New proposal			
Name of Main Applicant	Samuel Bernard		
Institution	Institute of Research on Ceramics (CNRS)	title	Dr

Aim of the research project

The scientific objectives of the present project were focused on the i) development of advanced knowledge on the design of sp^2 -BN with tailored crystallinity from BN precursors, and ii) the detailed investigation of the high pressure and high temperature treatment of these materials in order to produce c-BN, *i.e.*, sp^2 -BN, under mild conditions with the key property requirements; properties studied in details. These scientific (and also technical) objectives covered fundamental and applied aspects and propose to address the following key issue: Control of the crystallinity of precursor-derived sp^2 -BN; especially design h-BN *via* the chemistry of precursors modified with alkaline metals and generate sp^3 -BN (c-BN) at significantly lower temperatures and pressures than those reported in the literature. Within this context, the proposed research intended to investigate i) the synthesis of precursors of sp^2 -BN, ii) their reaction with molecular compounds containing the catalysts/additives that promote the formation of h-BN and c-BN such as lithium (Li), iii) the design of sp^2 -BN with tailored crystallinity and then iv) the high pressure/high temperature treatment (HP/HT) of materials prepared in iii) to form sp^3 -BN (c-BN).

Contents and results of the research

Ammonia borane (AB, $\text{H}_3\text{N}\cdot\text{BH}_3$) is a molecular solid generally used as hydrogen storage material due to its high hydrogen content (19.6 wt.%) as discussed in chapter 1. Here we look at its use as molecular precursor for synthesis of BN (Figure 1).

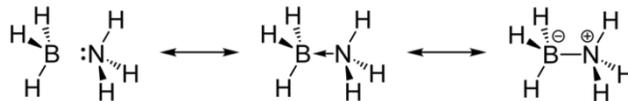


Figure 1 Resonance structure of ammonia borane (AB)

AB is a promising precursor for BN due to the fact that it has all the elements required to form stoichiometric BN and the only extra element to be removed is hydrogen. Figure 2 shows the FTIR spectrum of AB. Between 3200 and 3400 cm^{-1} we have the bands due to stretching of N-H bonds. The broad band centered around 2300 cm^{-1} corresponds to stretching of B-H bonds. Two sharp bands corresponding to deformation of N-H bonds appear at 1625 and 1375 cm^{-1} . Similarly bands due to the deformation of B-H bonds come up at 1170 and 1060 cm^{-1} . Finally, there are two intense peaks corresponding to stretching and rocking of B-N bond at 780 cm^{-1} and 740 cm^{-1} respectively. However, we should mention that in the literature B-N stretching has been also attributed to peaks at 1440 cm^{-1} , 1380 cm^{-1} and 850 cm^{-1} .

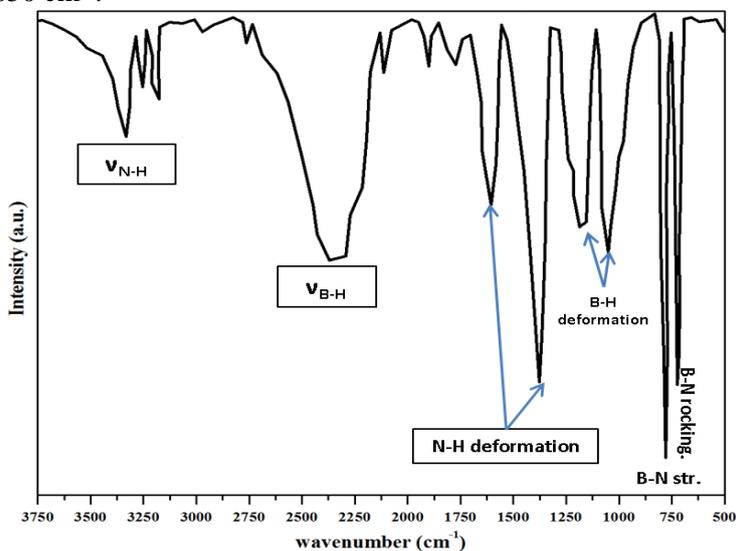


Figure 2 FTIR spectrum of AB

The pyrolysis of AB under NH_3 flow at 1000°C for 2 hours leads to a poorly crystallized sample we labeled **ABBN-1000** as shown in Fig. 3. By annealing the ammonia-treated sample at 1450°C under N_2 , we formed the sample labelled **ABBN-1450**.

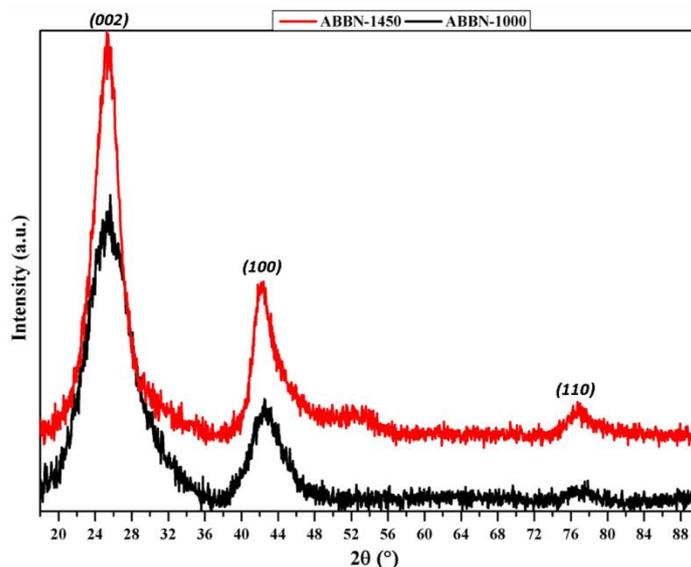


Figure 3 XRD of BN produced by pyrolysis of AB at 1000°C and 1450°C

Structural evolution of BN derived from ammonia borane was investigated using XRD as shown in Figure 3.3. The annealing was stopped at 1450°C because higher temperatures did not allow obtaining higher degree of crystallinity.

The XRD pattern of the **ABBN-1450** sample has broad and weak peaks emerging at 25.3°, 42.4° and 76.7°. The XRD pattern for **ABBN-1450** is similar to turbostratic BN (t-BN). The crystallite size calculated using Scherrer equation at the dominant (002) peak was found to be 2.73 nm which clearly indicates a very low degree of crystallization. It should be mentioned that two disordered BN phases, *i.e.*, turbostratic-BN (t-BN) and amorphous-BN (a-BN), are usually found in addition to the hexagonal phase. The turbostratic BN phase is characterized by a random stacking sequence of the (002) layers and a disorientation of these layers around the c-axis, whereas the amorphous BN phase represents a structure disordered at atomic level. XRD patterns of such phases are significantly distinct from that of h-BN. To significantly improve the degree of crystallization of AB-derived BN, we performed the reaction between AB and LiNH₂ in a ball milling reactor (solid state reaction) at 200 rpm for 4 hours. This process is called mechano-synthesis. The polymer (**ABLi1-BM**) powders obtained after this process have been pyrolyzed at 1000 °C under NH₃ then annealed up to 1450°C in flowing N₂. Figure 4 shows the XRD patterns of the **ABLi1-1000-BM** and **ABLi1-1450-BM** samples.

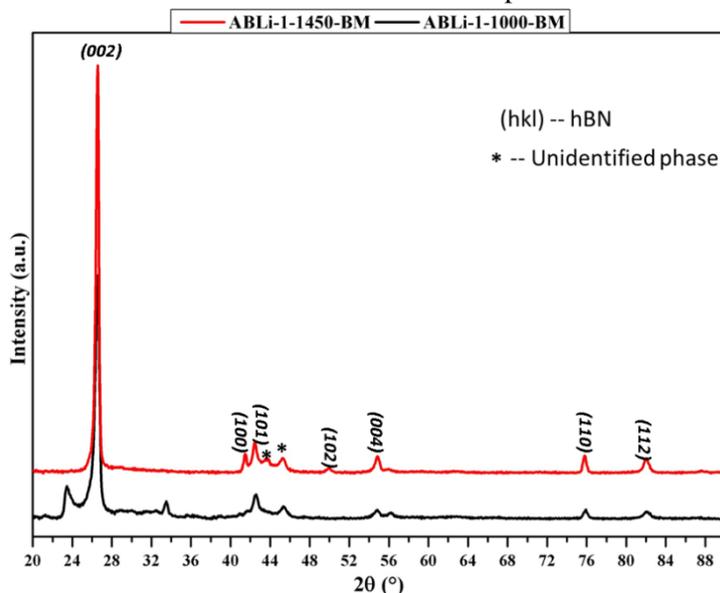


Figure 4. XRD patterns of the **ABLi1-1000-BM** and **ABLi1-1450-BM** samples

The crystallite size calculated at the dominant (002) peak using Scherrer equation was found to be 18.46 nm which upon annealing to 1450 °C (**ABLi1-1450-BM**) increased to 25.85 nm. Values above 17 nm generally indicate good degree of crystallinity. More interesting, the **ABLi1-1450-BM** sample crystallized as hexagonal boron nitride. The peaks were matched using JCPDS file number 04-003-6253. The most important peak which suggests the complete crystallization of BN at 1450 °C is the (102) peak. Therefore, we proved that reactive ball-milling is a promising approach to prepare highly crystallized BN at relatively low temperatures from *single-source* precursors. Interestingly, we could select the **ABLi1-1000-BM** sample for further investigations. This sample has been analyzed by Auger electron spectroscopy to determine the distribution in Li, B and N which was confirmed as shown in Figure 5.

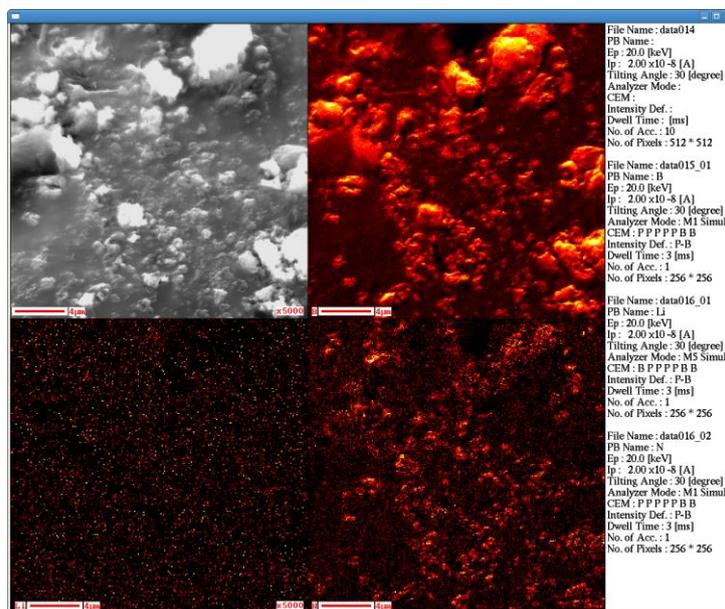


Figure 5. AES spectra of the **ABLi1-1000-BM** sample

Then, we investigated the high pressure and high temperature (HPHT) treatment at NIMS (Tsukuba, Dr. T.

Taniguchi) to form c-BN. It appeared that we formed a major phase of c-BN after HPHT of the **ABLi1-1000-BM** sample at 6.5 GPa and 1400 °C as shown by XRD (Figure 6). The XRD pattern of the **ABLi1-1000-BM_6.5-1400** sample indeed exhibited the (111), (220), (311), and (400) Bragg reflections of c-BN.

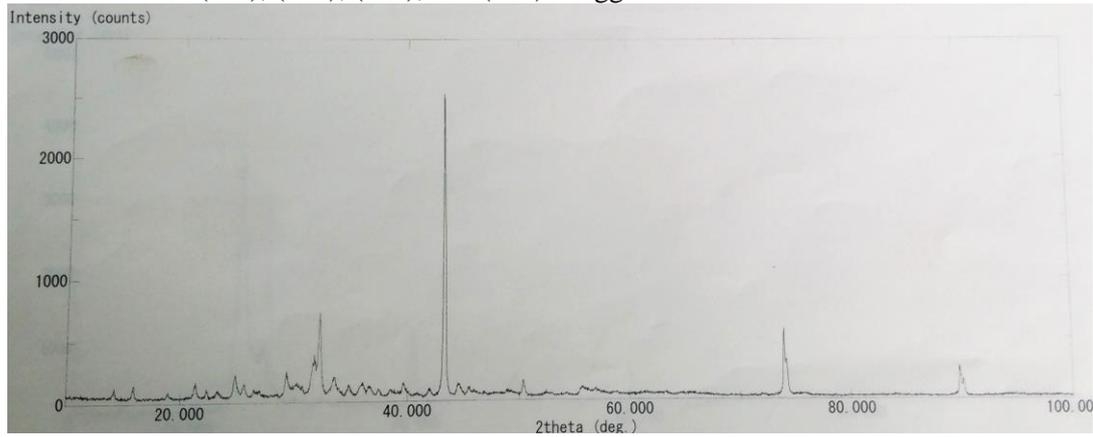


Figure 6. XRD patterns of the **ABLi1-1000-BM_6.5-1400** sample

Based on this result, we investigated TEM of the sample samples and we confirmed the formation of c-BN in the **ABLi1-1000-BM_6.5-1400** sample as shown in Figure 7.

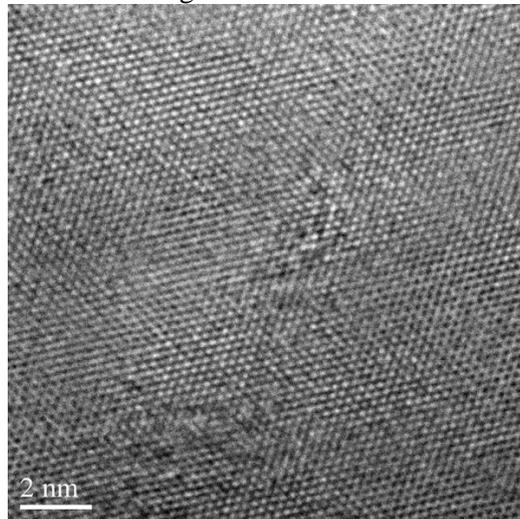


Figure 7. TEM image of the **ABLi1-1000-BM_6.5-1400** sample

Therefore, we were able to demonstrate the formation of c-BN by the modification of BN precursors at molecular scale using reactive ball-milling through the ZAIKEN project.