



	<b>Experiment title:</b> Complex high pressure phase transformation of nano alkaline boron carbides into superhard materials	<b>Experiment number:</b> CH-5789
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<b>Shifts:</b> 12	<b>Local contact(s):</b> Wilson Crichton wilson.crichton@esrf.fr	<i>Received at ESRF :</i> 07/09/2021
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## Introduction:

Superhard materials exhibit Vickers' hardness exceeding 40 GPa. Bulk diamond has remained the hardest known compound (70-120 GPa), until nanostructured diamond in the form of aggregated nanorods exhibited hardness values as high as 130 GPa. Diamond is extensively used as a cutting and working tool, but its cost and stability are severe limitations: diamond suffers oxidation above 800 °C and dissolves in iron to yield iron carbides. Boron carbides have emerged as promising substitutes. They share the high degree of covalence necessary (but not sufficient) for achieving very high hardness. Boron carbide ( $B_{4+\delta}C$ ) compounds have been largely studied because of their outstanding chemical and thermal stability combined with hardness lying within the superhard range.  $B_{4+\delta}C$  possess promising commercialization potential in the military, aerospace, and aviation fields, only impeded by the high-pressure brittle failure occurring by an amorphous shear band formation. Therefore, there is a strong research interest to seek the optimization and rationalization of mechanical properties in the B-C system.<sup>1</sup>

Several strategies have been proposed for tackling such difficulties. A first approach is to reduce the particle size down to the nm scale (*ca.* 10 nm), where so-called Hall-Petch strengthening takes place due to the increase in grain boundaries density.<sup>2,3</sup> Secondly, incorporation of a slight excess of carbon is theoretically expected to increase the hardness and fracture toughness.<sup>4</sup> Finally, recent modelling also suggests that alkaline dopants may strengthen  $B_{4+\delta}C$ , although such a strategy has not been reported experimentally.<sup>1</sup>

Our group has recently developed a new material ideally suited to tackle all the above-mentioned approaches at the same time: a compound of formula  $NaB_5C$ . The main goal of the current experiments is to explore the transformation of  $NaB_5C$  into  $B_{4+\delta}C$  structures under high pressure and high temperature.

## Experimental:

We performed systematic studies of HP-HT transformations in the large volume multi-anvil press with *in situ* angle-dispersive X-ray diffraction (1-D detector) for fast observation of phase transformations.

For our experiments, we employed 32 mm WC anvils. Pressure cells were made of MgO octahedrons, and an assembly composed of a heater (tantalum, Ta), plugs (MgO) and *h*-BN capsule in which sample powder was loaded. In order to collect time-resolved X-ray diffraction patterns, the beam passed between the second-stage anvils; "windows" inserts filled with amorphous boron:epoxy in the gaskets facilitate the transmission of X-rays. Throughout the run, "windows" into octahedron and gaskets were changed to diamond:epoxy due to the high signal of the former "windows" that were masking the sample diffraction. Also, Ta heater were changed to graphite due to oxidation of the heater. Actual gaskets and heaters used will be detailed for each sample.

**Because of the COVID pandemic situation and of ESRF restriction, this experiment was performed remotely.** Despite the extensive help of the beamline scientist, such an experiment is very difficult to conduct "in remote" mode. In principle, such experiments are scalable: each conclusion of an experiment makes it possible to modify and optimize the next set-up assembly for the following experiment. However, this was only partially possible here since, because of the "remote" mode, all our octahedra had been loaded in Paris and it was no longer possible to deeply modify the set-ups. Clearly, several difficulties encountered during this beamtime come from this constraint.

## Results and discussion:

The experiments performed during the run were designed to be exploratory. It was previously known that at high pressure,  $\text{NaB}_5\text{C}$  eventually transforms to boron carbide ( $\text{B}_{4+\delta}\text{C}$ ) if enough heat is applied. Our main goals for this experimental light were to shed light on the mechanism and possible presence of intermediate phases for the  $\text{NaB}_5\text{C}$  to  $\text{B}_{4+\delta}\text{C}$  transformation.

In a first experiment, we increased the pressure of the sample to 5 GPa and performed a temperature scan of  $50\text{ °C}\cdot\text{min}^{-1}$ . It was quickly evidenced that the environment surrounding the sample was contributing to a large background, which covered all possible signal from the material itself. This can be observed in Figure 1, where all the scans recorded are summarized in a 2D plot as a function of the angle. Only  $\beta$ -boron and hexagonal boron nitride, originating from the sample environment, are detected in the whole range of measurement.

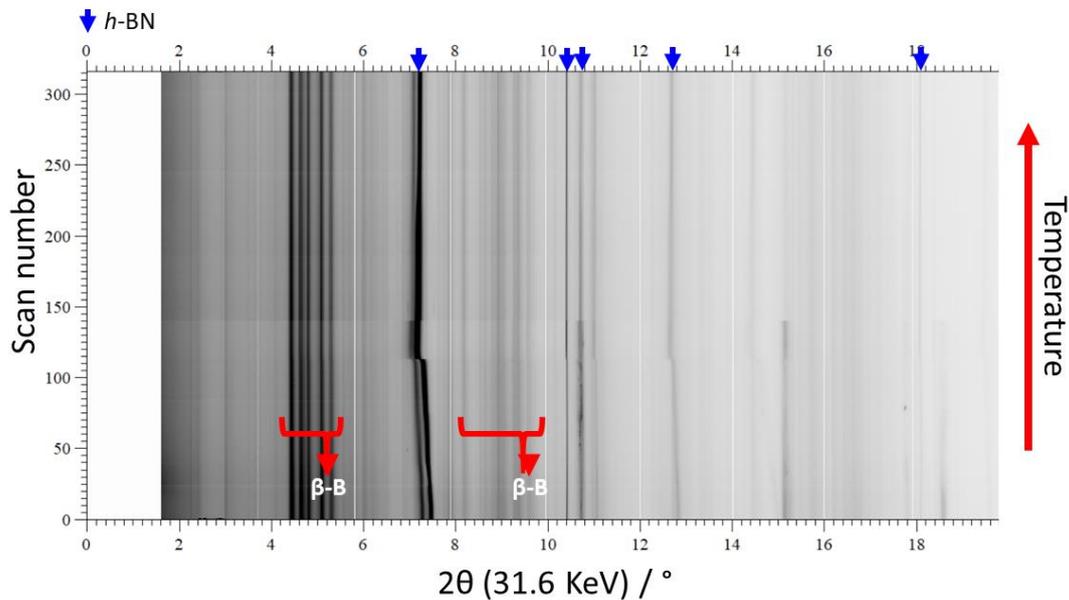


Figure 1. Diffraction signal at heat scan of  $\text{NaB}_5\text{C}$  at 5 GPa.

In order to detect the sample by reducing the background signal, the “windows” were changed to diamond:epoxy cylinders instead of the initial boron:epoxy ones. Likewise, the beam energy was increased to 52.67 keV, to enable larger transmission. Indeed, the change of configuration does allow detecting the most intense (110) diffraction peak from  $\text{NaB}_5\text{C}$ , as shown in Figure 2. Unfortunately, upon compression, the signal is masked by the (002) diffraction peak of  $h$ -BN as seen in Figure 3.

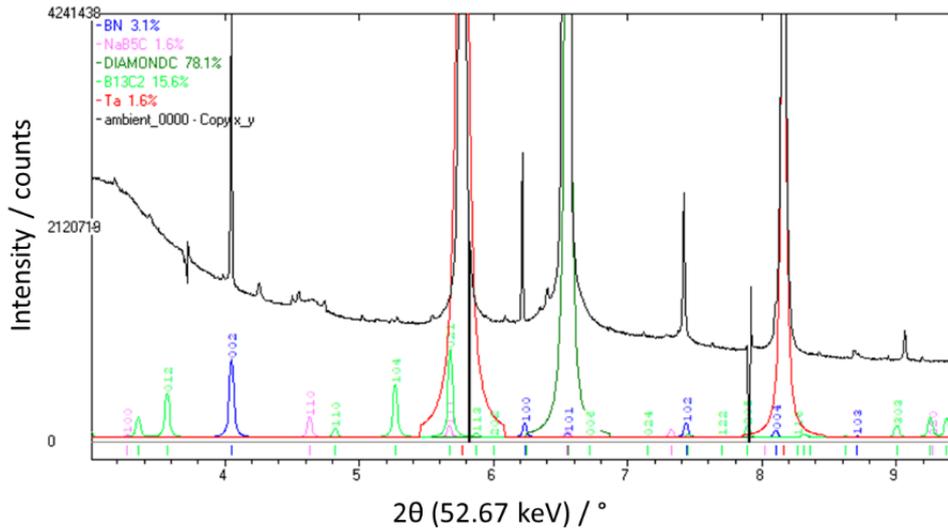


Figure 2. 1D diffractogram of NaB<sub>5</sub>C in diamond:epoxy gasket.

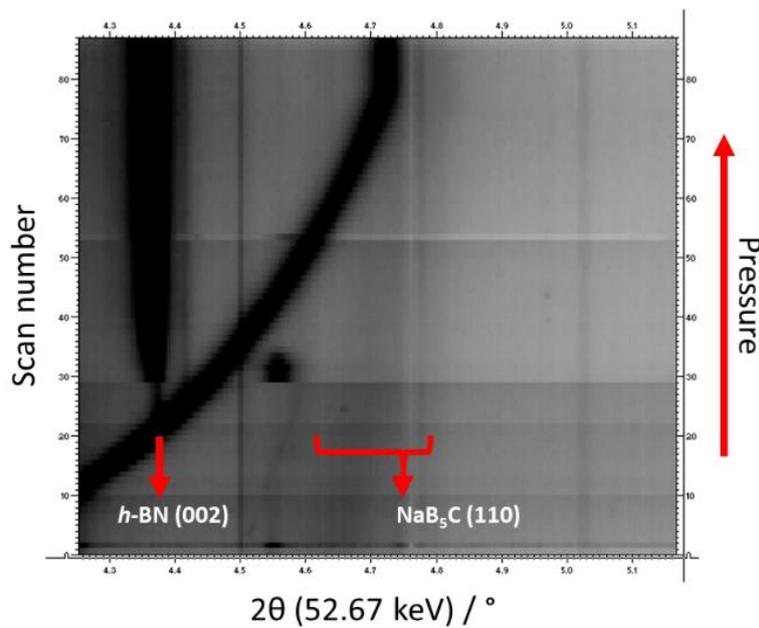


Figure 3. Diffraction scan while compressing NaB<sub>5</sub>C in diamond:epoxy gasket.

Yet, the temperature scan was still performed, as shown in Figure 4, where peaks corresponding to sample environment are marked with arrows. No significant change was observed until very high temperature (above 1500 °C), where a new family of diffraction peaks emerges. This region is marked in a red square in Figure 4. In order to identify the origin of these peaks, we recovered the sample after quenching, opened the assembly and recorded its diffraction pattern *ex situ*. Upon comparison between *ex situ* and *in situ* patterns (Figure 5), these new peaks do not originate from the sample itself but are ascribed to oxides of Ta (Figure 6), which is used as a heating element.

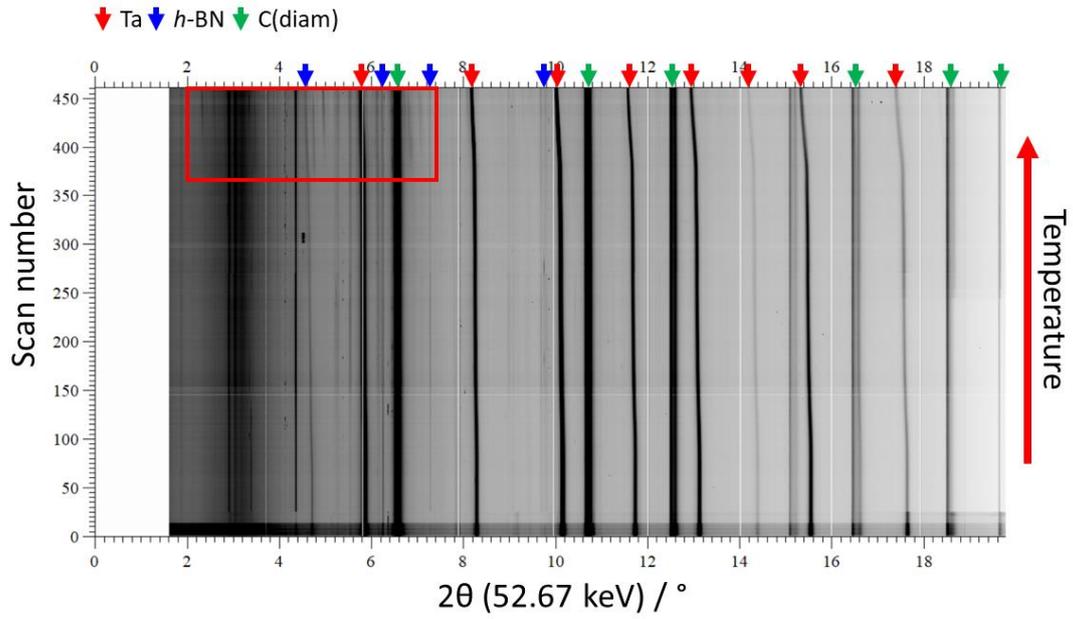


Figure 4. Diffraction signal at heat scan of  $\text{NaB}_5\text{C}$  at 10 GPa

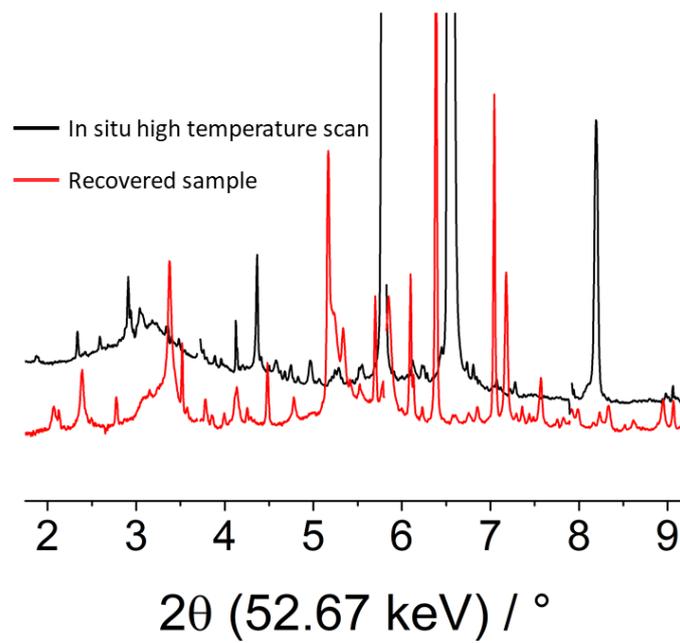


Figure 5. Comparison between the 1D *in situ* diffraction pattern after a new family of peaks appears, and an *ex situ* XRD pattern recorded from the recovered sample without environment.

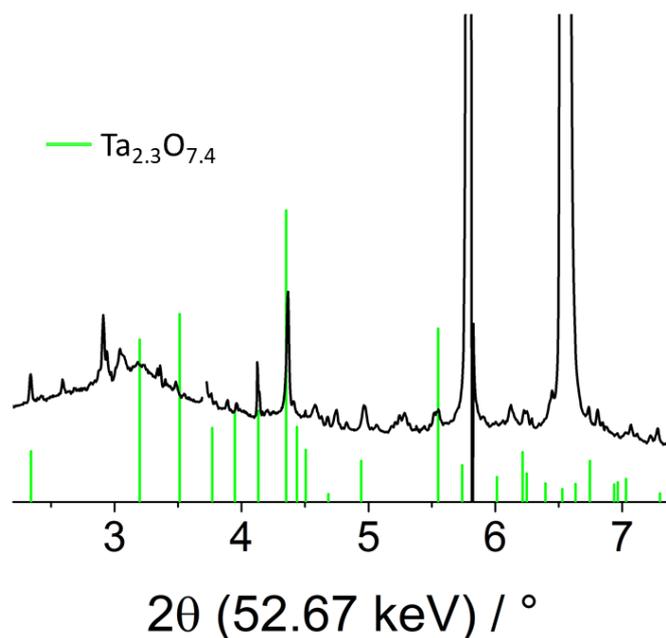


Figure 6. Indexation of the 1D *in situ* diffraction scan to a Ta oxide.

Regarding the recovered solid, two crystalline phases can be indexed:  $\text{NaB}_6\text{H}_6$  and  $\text{Na}_2\text{B}_4\text{O}_7$  (see Figure 7). The presence of both a reduced and an oxidized boron-sodium phase can be interpreted as a sign of partial poisoning of the sample, sustained by the fact that the Ta oven itself is being oxidized throughout the experiment. We can formulate the hypothesis that if enough oxygen can reach the sample at high temperature, the oxidation of the  $\text{NaB}_5\text{C}$  precursor can be triggered to yield the observed  $\text{Na}_2\text{B}_4\text{O}_7$  phase.

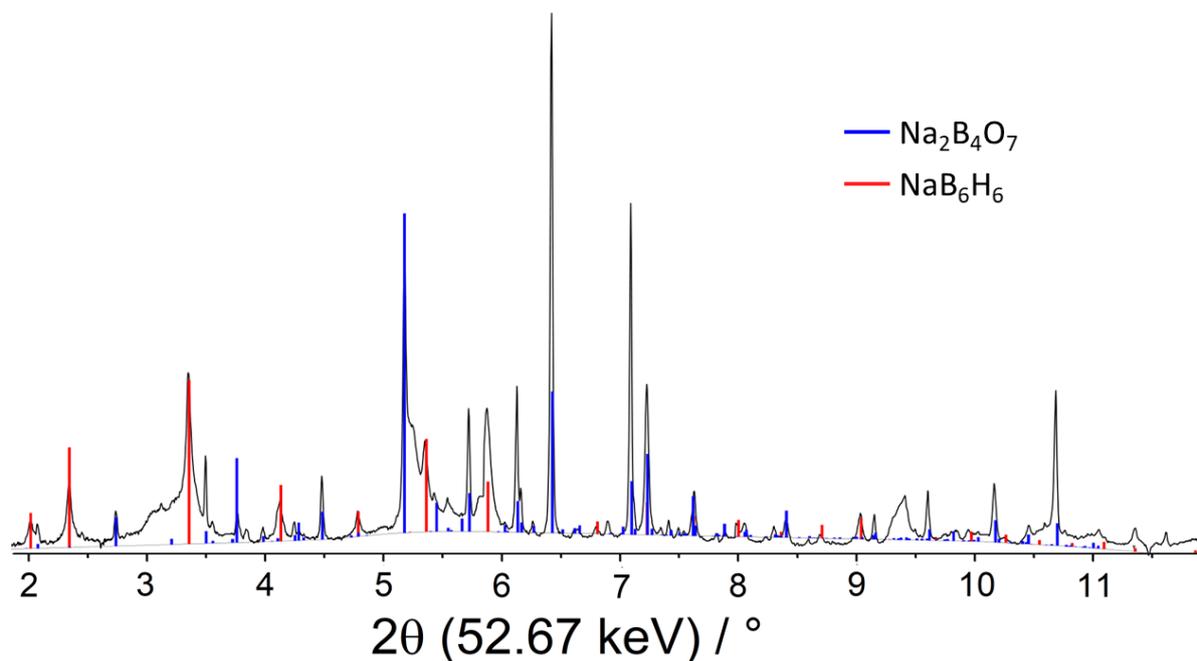


Figure 7. Indexation of the XRD pattern of a sample recovered after HP-HT treatment in a tantalum furnace.

At this point, we attempted to solve the problem of contamination by changing the Ta oven to graphite, which is itself less prone to oxidation and has much smaller Z number, thus enabling larger beam

transmission. A similar temperature scan was performed at 10 GPa, but still, no discernible sample signal was detected in the whole scan range (Figure 8). However, when the sample was recovered upon removal of the environment setup, the final thermodynamic phase of boron carbide ( $B_{4+\delta}C$ ) was detected (Figure 9), instead of the hydride/oxide mixture described above. This indicated that indeed the use of graphite instead of Ta enabled preventing sample contamination during the experiment. Unfortunately, since no high (P,T) *in situ* signal from the sample could be obtained, no further useful information could be recovered throughout the run.

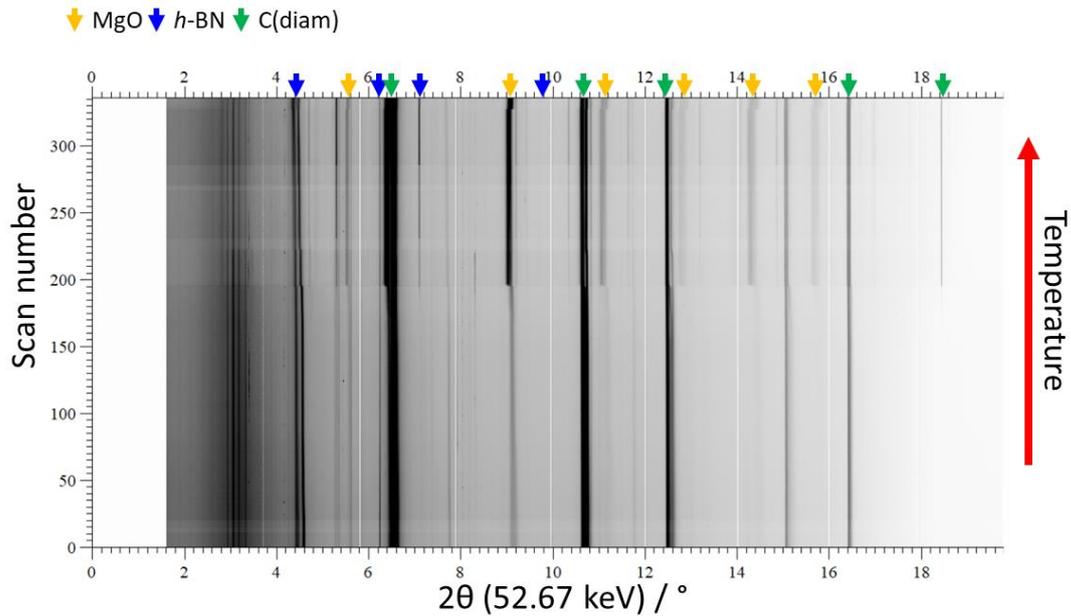


Figure 8. Diffraction signal during a heat scan of  $NaB_5C$  at 10 GPa in a graphite oven.

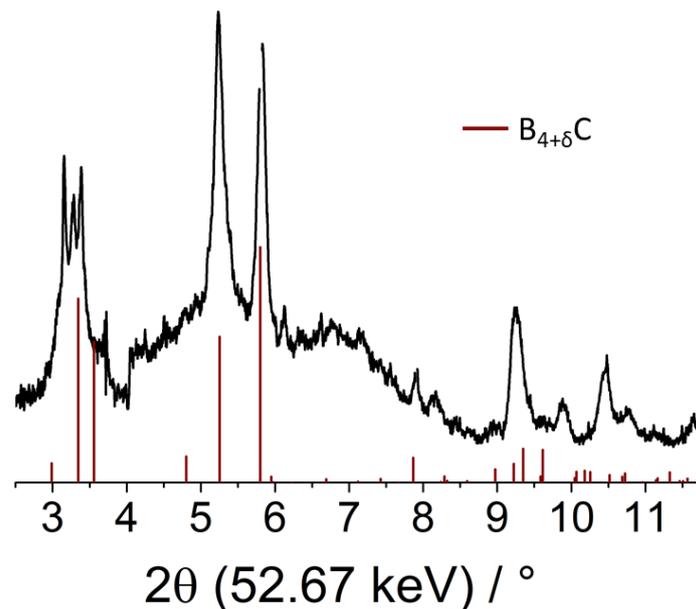


Figure 9. Indexation of the XRD pattern of a sample recovered after HP-HT treatment in a graphite furnace.

To conclude, this experiment was instrumental in identifying the stringent conditions and sample environment required to perform *in situ* X-ray diffraction for assessing phase transformation in light elements-based sodium boron carbide. Especially, further experiments will require the use of light and thin sample environments, strict atmosphere control, use of very high brilliance and penetrating X-ray beam, (if possible in the future) use of a Sollers slits' system and powerful detection system. The measurement conditions will be optimized, and their suitability controlled in the future.

### References:

[1]: He, Y., et. al. *J. Am. Ceram. Soc.* **2020**, 103, 2012.

[2]: V. L. Solozhenko et al. *Adv. Mater.* **2012**, 24, 1540.

[3]: Jouini, Z. et al. *J. Superhard Mater.* **2016**, 38, 66.

[4]: Li, J., et. al. *Materials.* **2018**, 11, 1.