



	Experiment title: <i>In situ</i> structural study of metastable states during boron crystallization at high-pressure	Experiment number: CH 6477
Beamline: ID27	Date of experiment: 04/04/2023 – 08/04/2023	Date of report:
Shifts: 12	Local contact(s): Mohamed Mezouar Gaston Garbarino	<i>Received at ESRF:</i> 11/09/2022
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Aim of the proposal

The goal of this proposal was to study the structural evolution of nanostructured boron at high pressures. Our group has developed a nanostructured form of amorphous boron, different from commercial amorphous boron, as it exhibits (1) only short range order, with no feature of crystallization according to diffraction techniques, (2) negligible oxidation (circa 5 % at.), and (3) a very small average particle size of 5 nm. This material appears therefore ideal to study how nanostructuring can modify crystallization pathways and phase diagrams. This is especially true for boron at high pressure, as this element exhibits a very rich allotropism, especially at high pressure where the covalent bonds that prevail with this element can be reorganized. To monitor these transformations, identify the final structures and the intermediates, our aim was to use *in situ* X-ray diffraction. The monochromatic beam and Sollers slits at ID27 are ideal to probe these evolutions *in situ* within a large volume Paris-Edinburgh press.

1. Set-up

We have employed the Paris-Edinburgh press available at ID27 and a beam energy of ca. 33 keV to probe the high-pressure assemblies in transmission mode. The assemblies had been loaded under inert atmosphere, with carefully dried and deoxygenated powders. The first 2 shifts of the experiment were dedicated to setting up and alignment of the press (**Figure 1**).

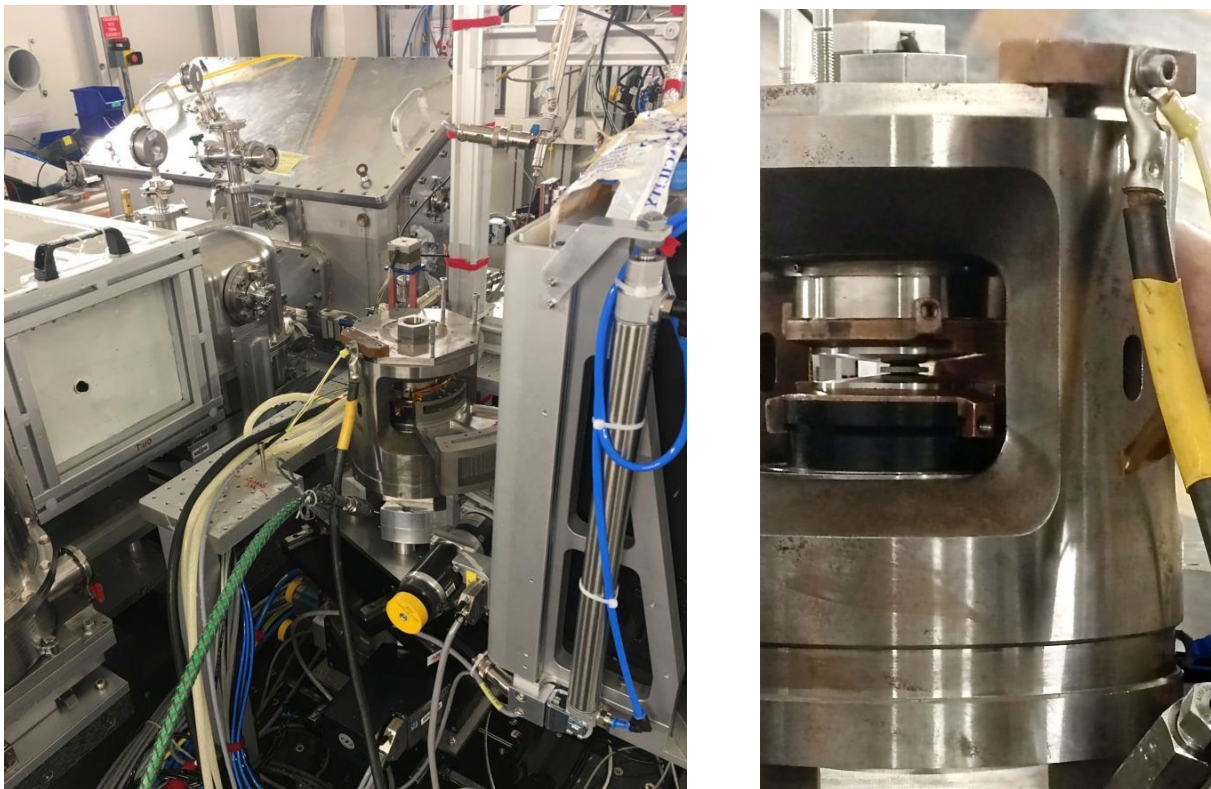


Figure 1. Paris-Edinburgh press installed on the ID27 stage.

2. Nanostructured boron allotropism at high pressure

Figure 2 depicts the XRD diagrams recorded during heating of nanostructured amorphous boron at 3 GPa. These diagrams are displayed as a heatmap, along the reaction time and temperature profile. We observe as major signal the diffraction peaks of *h*-BN, the capsule containing the amorphous powder. The cell parameters of *h*-BN are used to measure the pressure. The temperature is evaluated through a calibration curve determined prior to the experiment, but will be further refined with *h*-BN cell parameters.

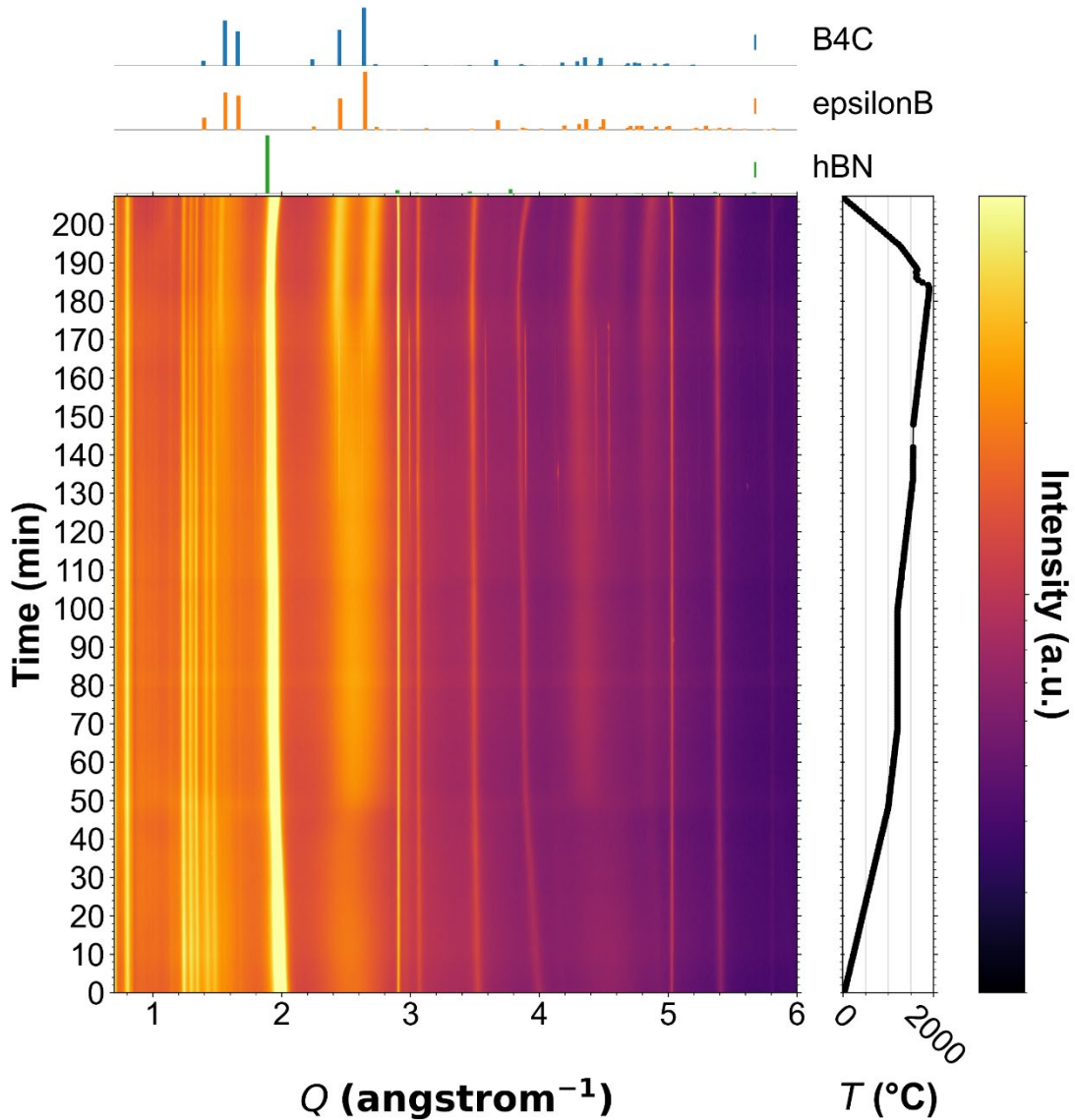


Figure 2. *In situ* XRD patterns shown as a heatmap along the temperature profile ($20\text{ }^{\circ}\text{C min}^{-1}$ heat ramps) during heating of a nanostructured amorphous boron powder at 3 GPa.

At the beginning of the reaction, the broad scattering at ~ 2.5 and 4.5 \AA^{-1} is ascribed to the initial amorphous boron material. At 48 min/ $1000\text{ }^{\circ}\text{C}$, the 4.5 \AA^{-1} contribution experiences a sudden shift to short Q values, reaching ca. 4.4 \AA^{-1} , while the initial 2.5 \AA^{-1} contribution shifts to large Q values (2.6 \AA^{-1}), as expected from thermal

dilatation. These two signals remain at constant values up to 140 min/2000 °C. Then, the 2.6 Å⁻¹ signal splits into two diffraction peaks, which are assigned to the B₄C-type structure, in which the ε-B allotrope also crystallizes. Other corresponding diffraction peaks are observed at 1.5, 4.35 and 4.8 Å⁻¹. The cell parameters of boron carbide and ε-B are close to each other, so that the diffraction peaks cannot be easily distinguished, but note that some peaks are strongly shifted compared to structural references (eg. at 2.7 Å⁻¹). Further Rietveld refinement will be necessary to decipher unambiguously the nature of the solid. However, one may note that the initial amorphous boron powder was carefully washed and dried to avoid the presence of adventitious carbonaceous species, possibly originating from the purification step. Overall, even if structural confirmation will be needed, a solid with B₄C-type structure is formed and most probably corresponds to ε-B, which is a rare boron allotrope, previously reported only at higher pressure. These measurements agree with previous data recorded at PSICHE beamline of SOLEIL, in energy dispersive mode, hence with a resolution that was not sufficient to probe the small peak shifts expected between boron carbide and ε-B. A second important feature of the experiment depicted in **Figure 1** is the crystallization at 120 min/1500 °C of a transient and unidentified phase with sharp diffraction peaks (ca. 1.8, 2.42, 2.6, 3, 3.15, 3.6, 3.9, 4.1, 4.42, 4.5 Å⁻¹), which disappear at 175 min/1900 °C.

A second experiment (**Figure 3**) was performed with a different temperature profile, by targeting directly the crystallization of this transient phase at 1500 °C. A similar structural evolution was observed, with the formation of the transient phase at 1500 °C. Further heating at 2000 °C leads to the crystallization of the distorted B₄C-type structure, as for the first experiment, but the transient phase is maintained up to 165 min on the 2000 °C plateau. We then attempted to quench the medium by stopping heating. The transient phase was maintained. Unfortunately, pressure quenching led to the destruction of this phase, presumably by amorphization.

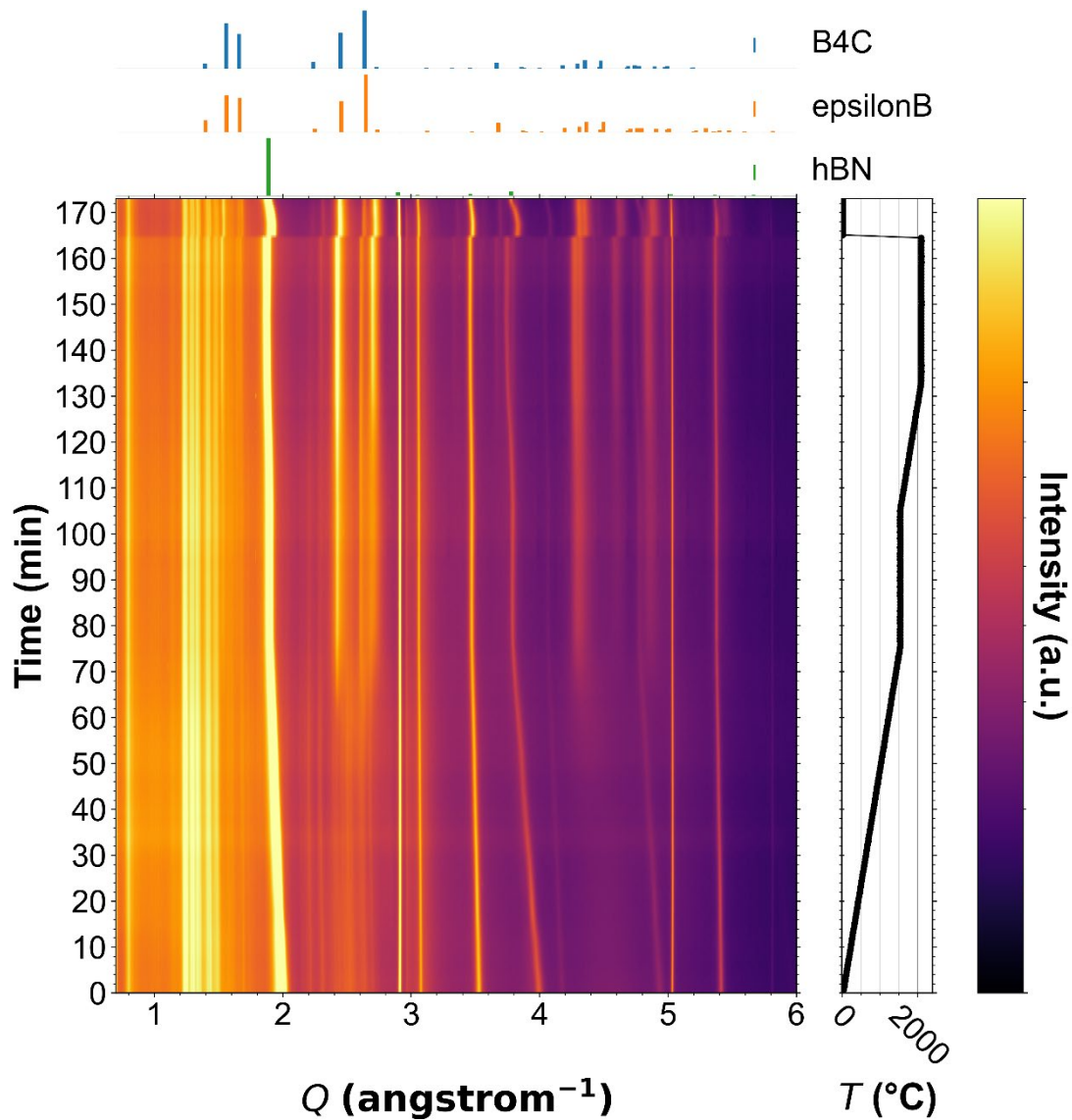


Figure 3. *In situ* XRD patterns shown as a heatmap along the temperature profile ($20\text{ }^{\circ}\text{C min}^{-1}$ heat ramps) during heating of a nanostructured amorphous boron powder at 3 GPa, targeting onset of crystallization of the transient phase.

As the first experiment encompassed several intermediate plateaus that increased the duration of heating and possibly favoured decomposition of the transient phase, and as the second experiment showed that this phase could be maintained at $2000\text{ }^{\circ}\text{C}$, we have then performed a third experiment at 3 GPa with direct heating at $2000\text{ }^{\circ}\text{C}$ (**Figure 4**), reached at 78 min. We observed crystallization from $1500\text{ }^{\circ}\text{C}$, as in the previous experiments. The transient phase was retained on the $2000\text{ }^{\circ}\text{C}$ plateau for ~ 45 min, possibly with the crystallization of the B_4C -type structure, which will require further confirmation. Again, temperature quenching enabled to maintain the crystal structure of the transient phase, but pressure quenching led to the loss of the phase. The high signal-to-noise ratio of the patterns acquired during this experiment, and the corresponding sharp diffraction peaks, are promising for further structural analysis, which will be performed in the near future.

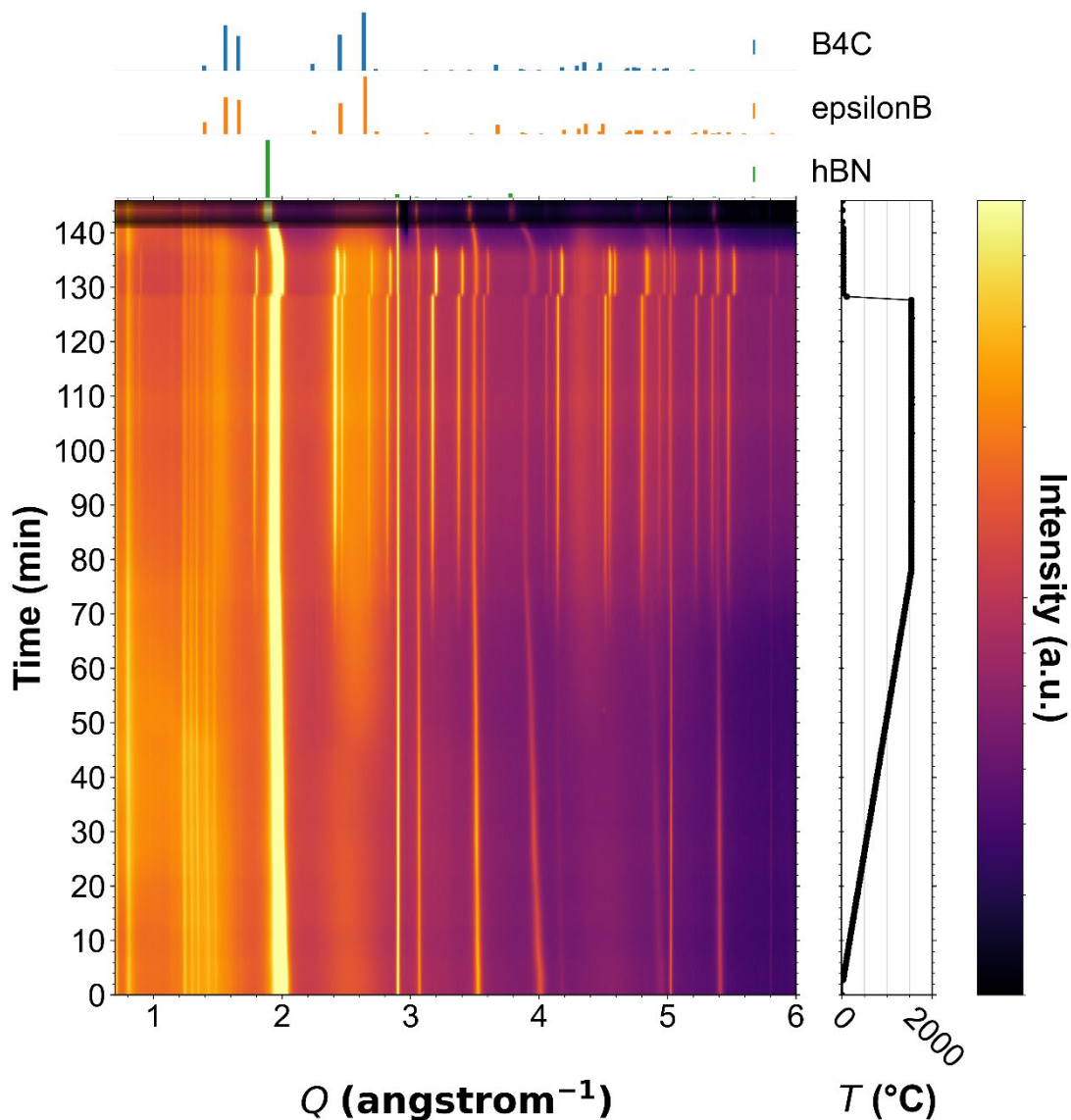
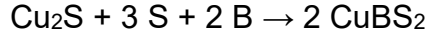


Figure 4. In situ XRD patterns shown as a heatmap along the temperature profile ($20\text{ }^{\circ}\text{C min}^{-1}$ heat ramps) during heating of a nanostructured amorphous boron powder at 3 GPa, targeting enhanced crystallization of the transient phase.

3. Extending the chemistry of boron to transition metals at high pressure

To follow up on structural transitions of boron, we have addressed the possibility to crystallize compounds of boron with metals that do not form boron compounds at ambient pressure. This is the case of copper, which does not exhibit any Cu-B compounds. Associating copper and boron is however highly promising to tune the charge state of copper and then its selectivity in the electrocatalysis of CO and CO₂ reduction. Using a ‘mediator’ element is a possible solution to combine Cu and B. CuBS₂ with zinc blende structure has been previously reported by Kajiki *et al.* in 2007 (T. Kajiki, Y. Hayashi, H. Takizawa, *Mater. Lett.* **61**, **2007**, 2382) through a synthesis at 2-3 GPa and 700-900 °C from Cu₂S, sulfur and boron, but its synthesis mechanism was not examined. For this reason, we have probed the reactivity of Cu with boron and sulfur together, according to the following reaction:



We have performed the experiment at 2 GPa. The evolution of the synthesis is summarised in the **Figure 5**. As temperature increases, we notice the formation of CuS and at about 300 °C, an intermediate phase forming which we indexed as B₁₂S. As temperature keeps increasing, the ternary phase CuBS₂ crystallizes at 700°C. we continued to heat up to 800 °C with a 30 min plateau to complete the reaction. The ternary phase could be recovered after pressure and temperature quenching, so that further investigation of the catalytic properties can now be envisaged. The present *in situ* study enables identifying the conditions of the crystallization onset. This will be of utmost importance to drive our efforts towards the synthesis of small (nano) grains of CuBS₂, with potential high surface-area for catalysis. We will then target the lowest temperature possible to limit grain growth.

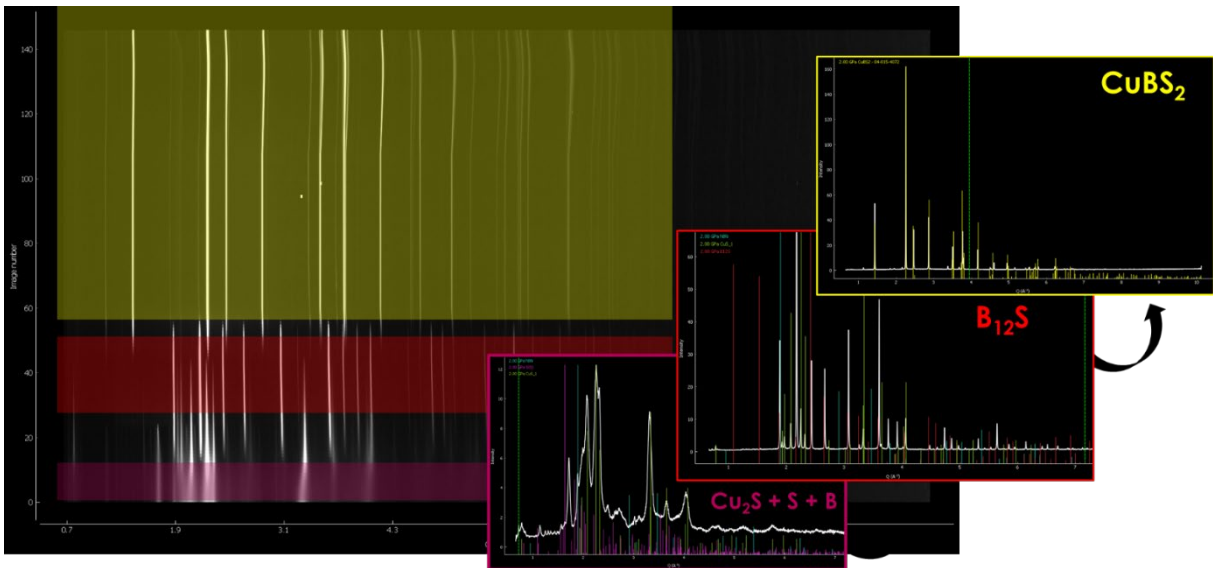


Figure 5. *In situ* XRD patterns shown as a heatmap along the temperature profile (20 °C min⁻¹ heat ramps) during heating of a Cu₂S:S:B (1:3:2 at. ratio) at 2 GPa, targeting CuBS₂. Selected patterns are shown as insets.

4. Conclusion and use of the beamtime

With this experiment, we were able to acquire high quality structural data that will facilitate the identification of the solid crystallized at high pressure from nanostructured amorphous boron: boron carbide, epsilon boron, or a distorted modification. We have also been able to identify the conditions of crystallization of a transient phase. This phase could not be recovered at room pressure, but the high-quality data we could obtain will be instrumental in the identification.

Overall the beamtime was operated smoothly, thanks to the great dedication of the local contacts. Setting of the experiment and of the temperature control required 2

shifts. We have experienced a difficulty that was related to a water leak from the cooling system of the hutch connected to the press. Solving this problem required about 1.5 shift. Again, we thank the local contacts for their great help.