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Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Single-crystal high-pressure high-temperature X-ray diffraction studies of boron carbide $B_{13}C_2$	**Experiment number**: HC-1635
Beamline: ID27	**Date of experiment**: from: 12-02-2015 to: 17-02-2015	**Date of report**:
Shifts: 15	**Local contact(s)**: Mohamed Mezouar	*Received at ESRF:*

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Report:

The aim of the proposed experiment was to perform the *single-crystal* high-pressure X-ray diffraction (XRD) studies of boron carbide, $B_{13}C_2$. Boron carbide is one of the most important superhard materials, since it possesses extremely high hardness together with remarkably low density. In this regard, a detailed structural analysis of boron carbide under high-pressure conditions is required in order to establish the interconnections between crystal structure, bonding scheme and mechanical properties. Single-crystal X-ray diffraction was chosen since it can provide very accurate structural details in comparison with powder XRD. Of particular interest is also the stability of $B_{13}C_2$ at high pressures and possible phase transitions or amorphization.

$B_{13}C_2$ were synthesized at 9 GPa and 1873 K in multi-anvil apparatus installed at Bayerisches Geoinstitut. Two high-quality single crystals of $B_{13}C_2$ together with a small ruby chip were loaded into a BX90-type diamond anvil cell equipped with Boehler-Almax diamond anvils (250 μm culet size). Ne was used as a pressure-transmitting medium. Pressure was determined using the ruby R_1 fluorescence line as a pressure marker and by measuring a position of the (111) X-ray diffraction line of Ne.

The sample was compressed up to ~70 GPa with a 4-7 GPa step size, at each pressure point the single-crystal XRD was collected. The XRD measurement was carried out in an angle-dispersive mode (λ = 0.3738 Å). Diffraction images were collected using a Perkin Elmer flat panel detector during 0.5° omega-scanning from -40 to +40°. To increase completeness of the dataset at several pressures the single-crystal XRD was collected from both crystals and the corresponding reflection intensities were merged. The data treatment (integration and absorption corrections) was performed with the CrysAlis RED software. The structures were solved by the direct method using the SHELXS software, full matrix least squares refinement on F^2 was performed by means Jana2006 software package.

The collected data demonstrated high quality. The experimental uncertainties in the cell parameters and the volume didn't exceed 0.1%. The Fig. 1*a*,*b* shows the volume and axial compressibilities, respectively. The preliminary fit by using the 2nd order Birch–Murnaghan EOS resulted in the following values: K_0 = 213(5) GPa, V_0 = 329.2(9) Å^3. While the calculated value of V_0 is in a good agreement with previously reported one (327.53 Å^3) [1], the estimated value of K_0 is smaller than the value of 231 GPa obtained in ultrasonic studies. Similarly to B_4C [3], the *c*/*a* ratio decreases during compression (Fig. 1*c*).

The inconsistency between the intensities of the equivalent reflections (R_{int}) was within 5%. High quality of XRD data allowed us to solve the crystal structure of $B_{13}C_2$ and refine the atomic coordinates and thermal parameters at each pressure point. The resulting discrepancy (R_1) between observed and calculated structure factors varied between 6 and 12%. No signs of phase transition or amorphization were observed. Figure 2 demonstrates that the crystal retains its quality up to the highest pressure reached. Currently we are analysing the structural data to follow pressure dependence of the bonds' lengths and angles and their influence on the axial compressibility and *c*/*a* ratio.

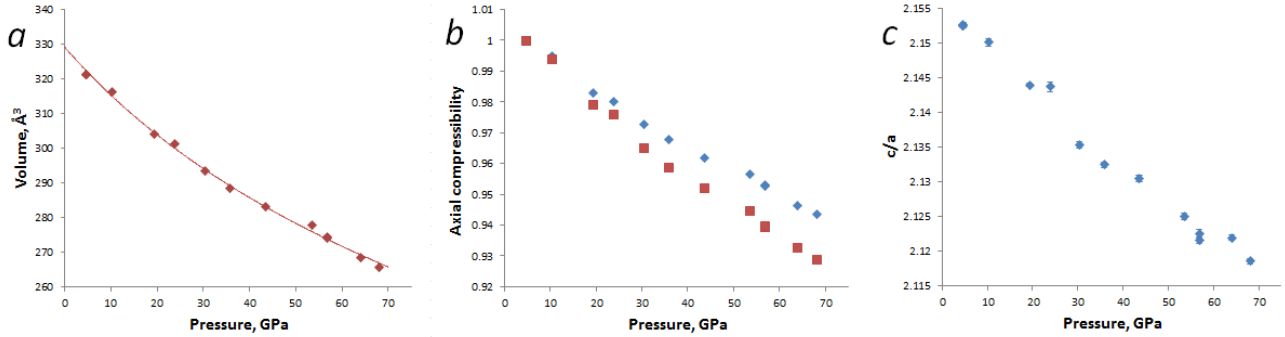

Figure 1. Volume (*a*) and axial compressibilities (*b*), and pressure dependence of *c*/*a* ratio (*c*) in $B_{13}C_2$. Solid line (*a*) corresponds to the fit with the 2nd order Birch–Murnaghan equation of state.

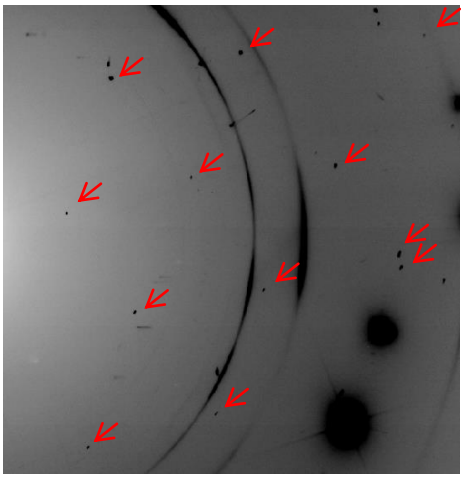

Figure 2. A fragment of the rotational image collected on $B_{13}C_2$ at 68 GPa. Arrows show the reflections belonging to the $B_{13}C_2$ single crystal.

We also made an attempt to synthesise *in situ* boron carbide by heating pure boron phases (α- and β-B) at pressures between 30 and 80 GPa using laser-heating set up installed by us (Fig. 3). In all cases only γ-B was obtained. In case of heating of boron in close proximity to the Re gasket we synthesised a novel boride, ReB_4, whose structure at about 70 GPa has been solved and refined.

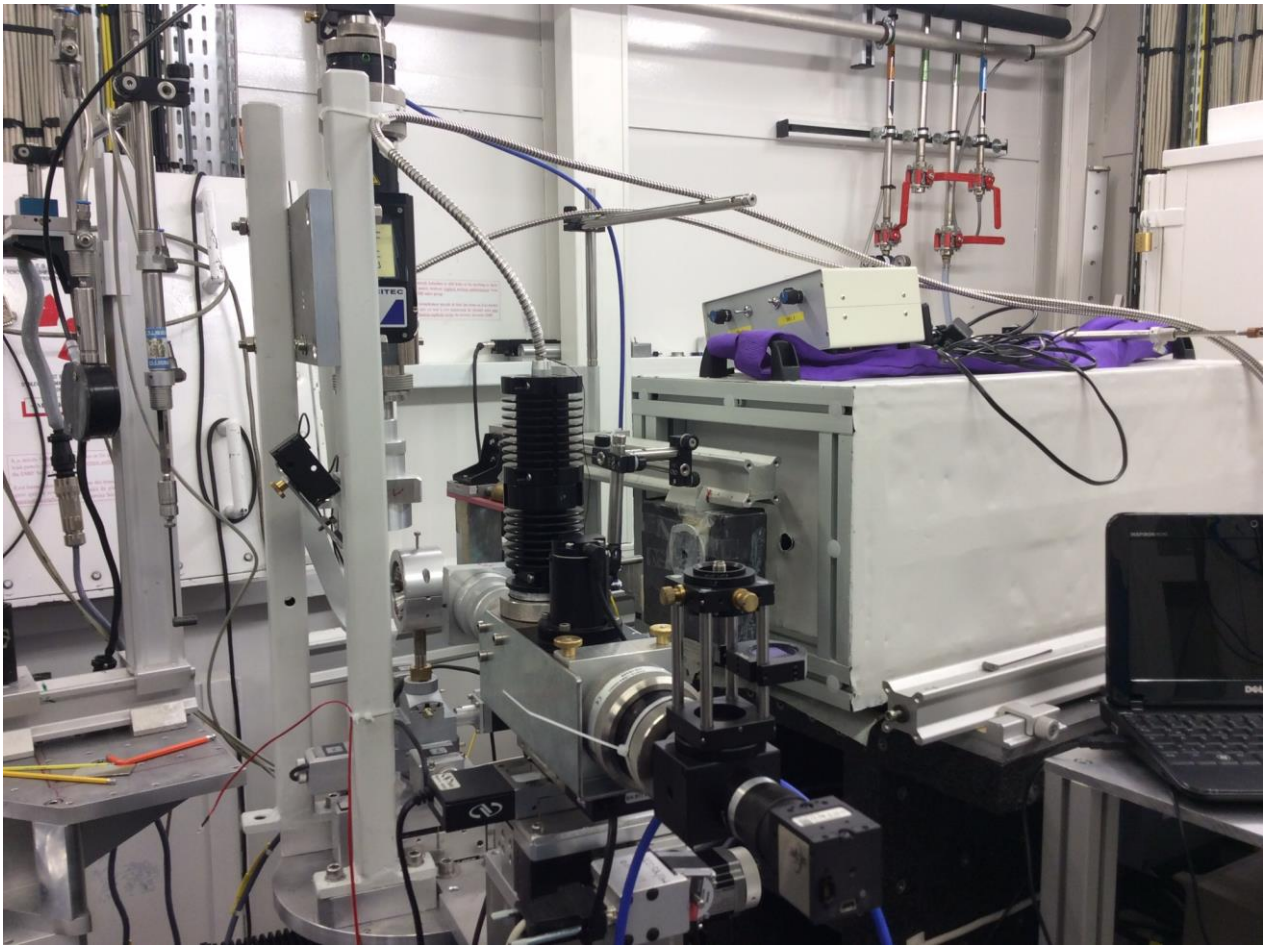

Figure 3. Laser heating set up for single crystal diffraction in DACs mounted at ID27.

While with help of the beam-line stuff we collected data of very high quality, some problems where identified: (a) the Perkin-Elmer detector has a too low dynamic range for the single-crystal diffraction data collection; (b) the acquisition time is about 30 min (*vs* about 5 min using MAR 555 detector at ID09a) and it greatly complicates high-temperature measurements; (c) at pressures above about 50 GPa the intensity of the incident X-ray beam is insufficient and its higher intensity would be highly desired.

References:

[1] Kwei, G.H. *et al.* Structures of the boron-rich boron carbides from neutron powder diffraction: implications for the nature of the inter-icosahedral chains. *J. Phys. Chem.* (1996), **100**, 8031.
[2] Gieske J.H. *et al.* Elastic properties of boron carbides. *AIP Conf. Proc.* (1991), **231**, 376 .
[3] Fujii, T. *et al.* X-ray diffraction study of B_4C under high pressure. *J. Phys. Conf. Ser*. (2010), **215**, 012011.