	Experiment title: Extending of Carbon Dioxide phase diagram for multi megabar pressure range	Experiment number: ES 963
Beamline: ID11	**Date of experiment**: from: 29.06.2021 to: 03.07.2021	**Date of report**: 11.09.2021
Shifts: 12	**Local contact(s)**: Eleanor Lawrence Bright	*Received at ESRF:*

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Report:

Objectives

The aim of this proposal was to utilize capabilities of ID11 beamline such as submicron focusing and ultra-high flux of X-ray beam to 1) perform high spatial resolution XRD mapping of the laser-heated CO_2 samples at pressures up to 200 GPa to build the phase distribution along the sample chamber of the DAC, 2) Allocate the regions of interest on the best crystallites of any detected phases and 3) collect high-quality single crystal XRD data of this phases to perform their structure solution and refinement. At present moment, ID11 is the only beamline that allows achieving these goals, especially with typically polycrystalline CO_2 samples, where the growing of single-crystalline domains with the size of above 1 um is barely possible. This study is important for the understanding of nature's most important molecular crystal due to its abundance in the Earth's, other terrestrial planets, asteroids, and other planetary bodies.

Results

Three large opening (90 degrees) BX90 type DACs with different culet diameters (80 to 250 μm) were prepared for this experiment. The CO2 samples were loaded in two of the DACs (80 and 250 μm culets) from the liquid phase using a homemade cryogenic loading system along with several pieces of Au for absorption of the laser radiation and dissipation of the heat to the CO_2 sample. The third DAC (250 μm culets) was loaded with the carbon disulfide (which has similar to CO_2 molecular symmetry at ambient conditions) along with pieces of Au. Au has the very well-established equation of state and it was used as a pressure gauge in all of our experiments. The CO_2 samples were compressed to target pressure of 51 (1) and 130 (3) GPa, and laser heated at our home laboratory equipment up to the maximum temperature of ~8000 K. Each of the CO_2 samples were heated with 3 different temperatures at different regions of the sample. The CS_2 sample was compressed up to 49(1) GPa and laser heated in a similar manner.

High spatial resolution X-ray diffraction maps of CO_2 sample at 51 GPa were collected and revealed the presence of well known tetragonal CO_2-V phase [1] (I-42d space group, figure 1.a) in all heated regions and no evidence of any unknown phases has been detected independently on the heating temperature. On the best positions of the map, single-crystal XRD datasets were acquired to establish the crystal structure of the CO_2-V phase (which was previously identified only with powder XRD). Similar results were obtained for the second CO_2 sample at 130 GPa (no evidence of phase transformation or decomposition of CO_2 - V were detected). Therefore, preliminary analysis of the temperature quenched samples shows, that the CO_2-V phase was found to be stable up to 130 GPa and 8300 (700) K. Analysis of the XRD data collected on the CS_2 sample at 50 GPa, shows that initially amorphous CS_2 (so-called Bridgamn's black polymer[2]) decomposes to carbon (in form of a diamond) and S-III with square chain structure [3] ($I4_1acd$ space group, figure 1.b). Table 1 summarizes the experimental conditions of the sample and observed results.

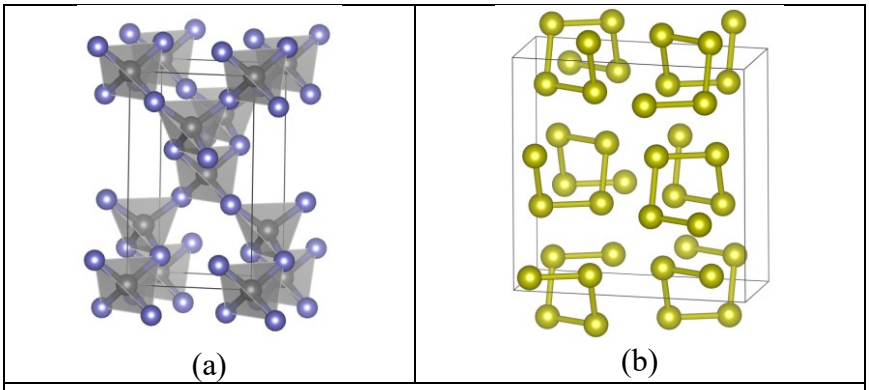

Figure 1. The crystal structure of CO2-V and S-III phases observed in the experiment.

Table 1. Preliminary results

Sample	Pressure, GPa	Temperature, K	Observed results
CO_2	130	2300 (200) 4600 (300) 8300 (700)	CO_2 - V remains stable
CO_2	5	2100 (200) 4300 (300) 8100 (600)	CO_2 - V remains stable
CS_2	49	2050 (150) 3850 (250) 4300 (300)	CS_2 -> Diamond + S-III

ID11 beamline allows to collect of high-quality single crystal XRD data for polycrystalline DAC samples. The intensities of the single crystal reflections were found to be very intense even for such light elements as C and O. However, proper alignment of submicron crystallites in the submicron X-ray beam and the center of rotation of the goniometer was found to be not trivial and time-consuming procedure. On-line preliminary single crystal data analysis is essential for such type of experiments, where 0.5 μm sample shift out of the goniometer center of rotation results in significant degradation of the collected SCXRD data. Despite this approach is time-expensive, at the present moment, it is the only strategy, to collect reliable SCXRD data on multimegabar DAC samples. Nevertheless, the beamtime was a great success and shows significant improvements of ID11 beamline at both: EBS-ESRF upgrade and local beamline upgrade from its hard- and software sides.

References

1. Datchi, F.; Mallick, B.; Salamat, A.; Ninet, S. Structure of Polymeric Carbon Dioxide CO2. *Phys. Rev. Lett.* **2012**, *108*, 125701, doi:10.1103/PhysRevLett.108.125701.
2. Whalley, E. structure of Bridgman's black carbon disulphide. *Can. J. Chem.* **1960**, *38*, 2105–2108, doi:10.1139/v60-285.
3. Degtyareva, O.; Gregoryanz, E.; Mao, H.K.; Hemley, R.J. Crystal structure of sulfur and selenium at pressures up to 160 GPa. *High Press. Res.* **2005**, *25*, 17–33, doi:10.1080/08957950412331331682.