EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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:** Synthesis of single-bonded crystalline polymeric carbon monoxide upon laser heating at megabar pressures	**Experiment number**: CH-6151
Beamline: ID-27	**Date of experiment**: from: 17 Jun 2022 to: 20 Jun 2022	**Date of report**: 22/08/2022
Shifts: 9	**Local contact(s)**: Mohamed Mezouar, Anna Pakhomova	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

In this experiment, we aimed to characterize the high pressure behaviour of poly-carbon monoxide (p-CO) under laser heating using CO_2 laser. Our previous XRD and IR studies showed how poly-CO was stabilized up to 50 GPa in an extended 3D network of mostly single-bonded carbon atoms, in good agreement with the previous theoretical calculations. These same calculations predicted the stability of crystalline pCO phases that were never experimentally synthesized due to the probable kinetic hindrance of the amorphous-crystalline transformation. This experiment was thus designed with the twofold purpose of 1) extending our previous XRD and IR results on amorphous poly-CO to higher pressure (possibly exceeding the Megabar) and 2) verifying the possibility to obtain crystalline poly-CO following laser heating (1000-4000 K) at very high pressure.

We cryo-loaded the CO samples at LENS, using three DACs provided by ESRF. The DACs were equipped with diamond anvils suitable to perform compression and laser heating on three samples up to 60-80 GPa (experiment 1CO, 250 μm culets) and up to 120-150 GPa (experiments 2CO and 3CO, 150/300 μm culets). We preindented and drilled the sample chambers into Re gaskets that were afterwards gilded with gold by Au sputtering in ESRF, so to protect the sample avoiding as much as possible its direct contact with the metal (Re) in order to exclude any catalytic effect during the experiments. We prepared the three samples with initial pressures of 30 GPa (1CO), 37 GPa (2CO) and 22 GPa (3CO). The formation of poly-CO was checked by Raman spectroscopy and visual inspection of the samples prior to begin the experiment in ESRF.

The 1CO sample was compressed to 50 GPa, and then laser heated at this pressure several times with increasing incident power. The coupling of the laser with the target poly-CO was not very good, and no major changes were observed in the XRD patterns. Using almost full power of the CO_2 laser we eventually obtained a better coupling and a transformation in the sample; nevertheless, the poly-CO sample seemed to decompose rather than crystallize, and this was attested by the appearance of the characteristic XRD pattern of CO_2-V, the

crystalline phase of CO_2 that is stable at this pressure conditions. Unfortunately, we lacked a reliable temperature measurement for this threshold.

To better characterize the temperature condition of the poly-CO decomposition we compressed the sample for the 2CO experiment up to 50 GPa and laser heated it again at this pressure. Pressure increased upon heating up to about 70 GPa, but we observed again the CO2-V signatures in the XRD pattern acquired after laser heating, and we measured the temperature as comprised between 3150 and 3400 K. Upon a subsequent heating at higher laser power (resulting in a further pressure increase up to 75 GPa), we reached a temperature of about 3600 K and succeded in further converting the remaining poly-CO into its decomposition products (CO_2-V and C, this one yet not being visible in the XRD patterns and probably amorphous).

The last sample (3CO) was compressed to Megabar (about 100 GPa) and laser heated at this conditions. We performed three different laser heatings with increasing incident laser power, and we observed a far better coupling, reaching temperature between 2400 and 2800 K (final pressure reached about 120 GPa). We did not observe any signature of a crystalization of poly-CO in these conditions. To improve the laser coupling with the target, we tried to decompress down to 85 GPa and to perform further heatings at this pressure. Here we reached higher temperatures (up to 4000 K) but we did observe nothing else than the comparison of Bragg peaks that can be related to CO_2-V, thus again attesting for the decomposition of poly-CO.

The results of these experiments pose some constraints to the future simulations on this system, evidencing how amorphous poly-Co tends to decompose into CO_2 and C instead of undergoing conversion in a stable, crystalline form. The kinetic hindrance of the conversion process seems therefore to be much higher than the kinetic barrier towards the decomposition. Despite we carefully prepared and gilded the Re gasket with gold, it is not clear if Re could have been involved and had some catalytic effect on the decomposition process (Re gaskets was gold-sputtered to protect them, but the very thin Au layer of about 100 nm could have been damaged in the various steps of the cell preparation and sample loading).

We are currently analyzing the XRD data obtained from these experiments. Moreover, we brought one cell back to LENS to measure Raman spectra on the obtained product (decomposed poly-CO) during decompression.