

Preparation and characterization of solid carbon monoxide at high pressure in the diamond anvil cell

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Over two decades ago, it was discovered that upon isothermal compression near 6 GPa carbon monoxide undergoes a phase transition to a polymeric phase at room temperature. Since this early report, the high pressure/high temperature phase diagram of carbon monoxide has been derived to modest pressures (15 GPa) and temperatures (600 K). The chemical and physical properties of quenched polymeric CO (poly-CO) have been extensively studied, but determination of the structural characteristics is still lacking [1-5].

Interestingly, previous thermochemical and vibrational studies have shown immense variation in the physical and chemical characteristics of the recovered poly-CO samples, which are strongly dependent upon the pathway of formation and the pressure from which it was quenched. This suggests that there may be several different forms of the polymeric material, similar to the low and high density forms of amorphous ice. Additionally, previous high-pressure synthesis and investigations of the physical and chemical properties of polymeric carbon monoxide have utilized only pure carbon monoxide gas and no hydrostatic pressure medium. It has been suggested that the addition of a pressure transmitting medium will limit the deviatoric stress in the sample and allow crystallization to occur.

Preparation of poly-CO samples: We loaded a mixture of 25 vol% carbon monoxide in 75 vol% helium in Boehler Almax diamond anvil cells (DAC) using the Frankfurt gas loading system. During compression of the gas mixture, the CO phase separated from the helium at around 3.5 – 3.8 GPa. The polymerization was induced photochemically at 5.2 GPa with a blue laser. Laser heating with a CO₂ laser between 6 and 7 GPa caused an unexpected phase transformation to a phase referred to as “white phase”. Poly-CO can be quenched and recovered to ambient conditions.

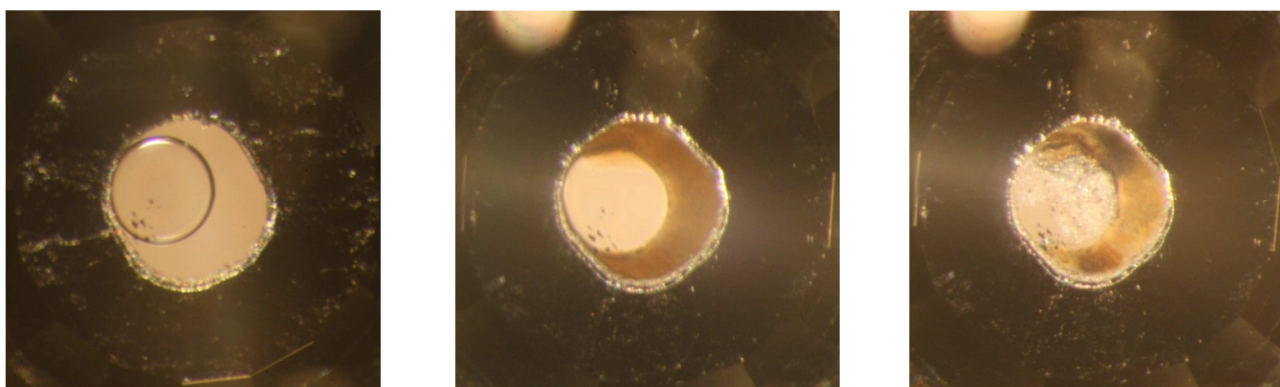


Figure 1: Left: Phase separation of CO and He (bubble) in the DAC at 3.5 GPa. Centre: poly-CO and He in the diamond anvil cell at 5.2 GPa. Right: “White phase” obtained after heating with a CO₂ laser at around 7 GPa.

Experiments: We performed in-situ X-ray diffraction at room temperature at the Laser Heating station in the Extreme Conditions Beamline P02.2. A Kirkpatrick-Baez focused beam of $2 \times 2 \mu\text{m}$ at an energy of 42.75 keV was used. Recovered samples and two different cells pressurized to 4.8 respective 6.8 GPa were used in the experiments.

In a first step we mapped the sample areas using the PerkinElmer XRD 1621 detector. In the area of the poly-CO we collected diffraction patterns optimized for PDF analysis. For the unknown “white phase” a single crystal data set was collected using the Mar345 imaging plate detector.

Analysis: PDFs of poly-CO were obtained using standard data reduction procedures (Software: *PDFgetX2*, $Q_{\max} = 12 \text{ \AA}^{-1}$) [6]. The scattering of the sample was very weak, which resulted in an unfavourable signal to noise ratio and unwanted oscillations in the PDF. There are a few structural peaks in the PDF though, which correspond to typical C – C and C – O distances to first and second neighbours, respectively. These structural peaks appear at around 1.33 and 2.47 Å. As expected, the PDF of poly-CO does not contain any structural features after 5 – 10 Å, since this is an amorphous material. No structural model has been found yet; the modelling is still in progress.

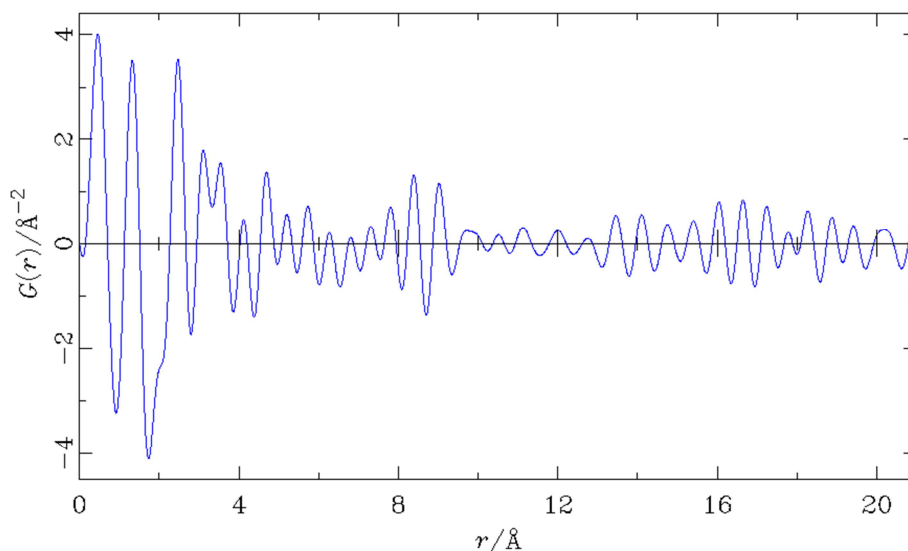


Figure 2: Experimental PDF of recovered poly-CO.

The analysis of the single crystal data is still on-going: the unknown phase is polycrystalline and the diffraction images are difficult to index.

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