



	Experiment title: Structural study of the pressure-induced reactivity of urea	Experiment number: CH 4708
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Shifts: 9	Local contact(s): Andrew Cairns	<i>Received at ESRF:</i>
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Report:

Urea is a simple molecular compound composed of light elements and a common nitrogen excretion product of animals, produced daily in huge quantities. Since its low cost and ready availability it found a variety of applications as a nitrogen-release fertilizer and industrial raw material. Interestingly, pyrolysis of urea lead to different products depending on the reaction conditions: while in an open vessel a mixture of simple molecular species is obtained, direct heating of urea in a closed container yields graphite-like carbon nitride exhibiting photocatalytic activity. The phase diagram of urea, however, has not been studied in detail (except for the low-pressure range investigated by P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, 1916, 52, 91-187) and its reactivity under pressure remains to date largely unexplored.

In the present experiment we investigated crystalline urea at high temperature and pressure conditions up to the reaction boundary, in order to shed some light on its phase diagram and the crystal structure of the phases, whose decomposition at HP/HT may lead to useful products. Therefore, we decided to load one powder and two single crystal samples into the diamond anvil cells using neon as a pressure transmitting medium. The rationale for using single crystals was to reveal if the crystal can remain intact through the phase transition, which might be beneficial for the subsequent structural determination of new crystal phases.

1. The first single crystal was heated and compressed avoiding crossing the I-III phase boundary (see the inset in the Figure). At *ca.* 400 K / 0.69 GPa the I-II phase boundary was traversed. A visual inspection of the sample disclosed that the crystal turned dark and the diffraction image at 400 K / 1 GPa showed that it shattered into smaller crystallites resulting in a powder pattern of Bridgman's phase II. After cooling down the cell to room temperature while keeping the pressure at 1 GPa, the powder pattern was indexed as phase III. The sample finally returned to phase I on pressure release to ambient.

2. The second single crystal experiment was performed by crossing the I-III phase boundary at room temperature. It resulted with a single-crystal to single-crystal phase transition,

although the quality of the single crystal in phase III was much deteriorated, with considerably increased mosaicity. At 1.5 GPa we started to raise the temperature. The reflections of Bridgman's phase II began to form at 378 K, but the complete transformation was achieved finally at 408 K. The sample was then cooled down taking care to keep pressure constant. The transition to phase III was observed at 1.3 GPa and 310 K; analogously to the previous experiment, the sample turned back to phase I on pressure release to ambient.

3. The powdered sample was compressed at ambient temperature up to 4.1 GPa observing the changes in diffraction patterns consistent with I→III and III→IV transition sequence. The diffraction pattern at 4.1 GPa reflects the coexistence of both phase III and phase IV. At this pressure the sample was heated up to 422 K, without substantial changes in the XRD patterns. Subsequently, pressure was released while keeping temperature constant at 422 K. The peaks corresponding to phase III eventually disappeared at 2.3 GPa. At this point, the temperature was slowly released not fully compensating a small pressure drop to 1.4 GPa at room temperature. Finally, phase IV was further compressed at room temperature. A clear change in the pattern was observed to begin around 6 GPa and complete around 8 GPa, in accordance with the previously reported IV→V phase transition. It should be stressed that the identification of phases III and IV was fully confirmed by the Rietveld refinement.

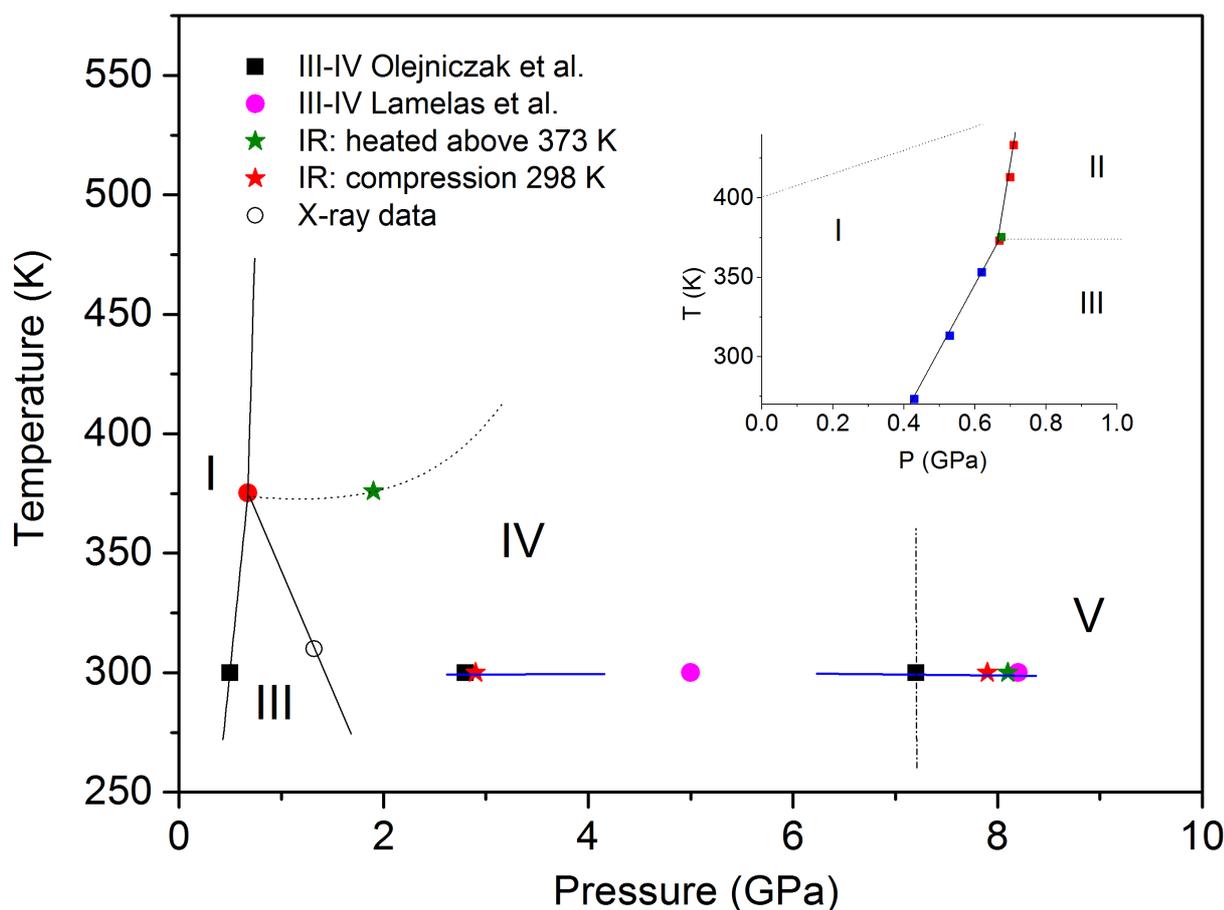


Figure. The revised phase diagram of urea based on the literature XRD (Olejniczak *et al.*) and Raman (Lamelas *et al.*) room temperature data and our HT-HP infrared absorption and XRD measurements. The inset shows the low-pressure part of phase diagram as proposed by Bridgman (1916) using volumetric data.

To sum up, we revised the phase diagram of urea, revealing that Bridgman's phase II and phase IV are actually the same phase and determining III-IV phase boundary. We have also determined equation of state of phase IV for the first time. Still, the structure of phase V and IV-V phase boundary remain unknown, and need to be explored in the future experiments.