ESRF	**Experiment title:** Thermal and mechanical properties of carbon dioxide at high pressures and temperatures	**Experiment number**: HS-763
Beamline: ID-30	**Date of experiment**: from: Nov. 25, 1998 to: Nov. 30, 1998	**Date of report**: Feb. 17, 1999
Shifts: 15	**Local contact(s)**: Carlson Stefan and Daniel Hausermann	*Received at ESRF:*

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Report:

Application of high pressure alters the nature of chemical bonds, electronic and crystal structures, and thermal and mechanical properties of solids. It has also been suggested that simple molecular solids may transform into a polymeric phase before they become metals at high pressure. Theoretical models and experimental data support this hypothesis, including polymeric forms of N_2, CO, diamond, β-C_3N_4, and symmetric-H_2O. Furthermore, these pressure-induced changes often occur in systematic ways, providing new routes for designing and synthesizing novel materials with advanced optical and mechanical properties. The structures of the N_2-polymer, diamond, and β-C_3N_4 at high pressures, for example, can be viewed as similar to the assemblages of heavier elements of each periodic group, P, Si, β-Si_3N_4 at low pressures, respectively.

In our recent Raman studies [1], we have discovered an extended-solid phase, CO_2-V, synthesized in a diamond-anvil cell by laser-heating the molecular orthorhombic phase, CO_2-III, above 40 GPa and 1800 K. This new material can be quenched to ambient temperature above 1 GPa. The vibration spectrum of CO_2-V

is similar to that of the quartz polymorph of SiO_2, indicating that it is an extended covalent solid with carbon-oxygen single bonds. This material is also optically nonlinear, generating the second harmonic of Nd:YLF laser at a wavelength of 527 nm with a conversion efficiency near 0.1 %.

The objective of the past run in FY98 at the ESRF was thus to characterize the crystal structure and its bulk mechanical property of CO_2-V at high pressures. Because CO_2 is made of relatively low-Z elements and the product CO_2-V is located in a small area of the sample at high pressures above 40 GPa, it was essential to use a highly bright synchrotron x-ray source available at the third generation synchrotron source. Furthermore, angle-resolved x-ray diffraction combinded with a fast scanning image-plate detector was very well suitable for characterizing highly preferably oriented crystal structures of CO_2 phases and determining their bulk properties such as the equation of state.

In this past run, by using the beamline ID-30 at the ESRF we have completed the structural analysis of seven samples: four samples being converted to CO_2-V at various P,T conditions and three untransformed CO_2-I and III samples. The diffraction patterns of various CO_2 phases, including CO_2-I, III and V were obtained to 60 GPa as shown in Fig. 1(a), (b) and (c), respectively.

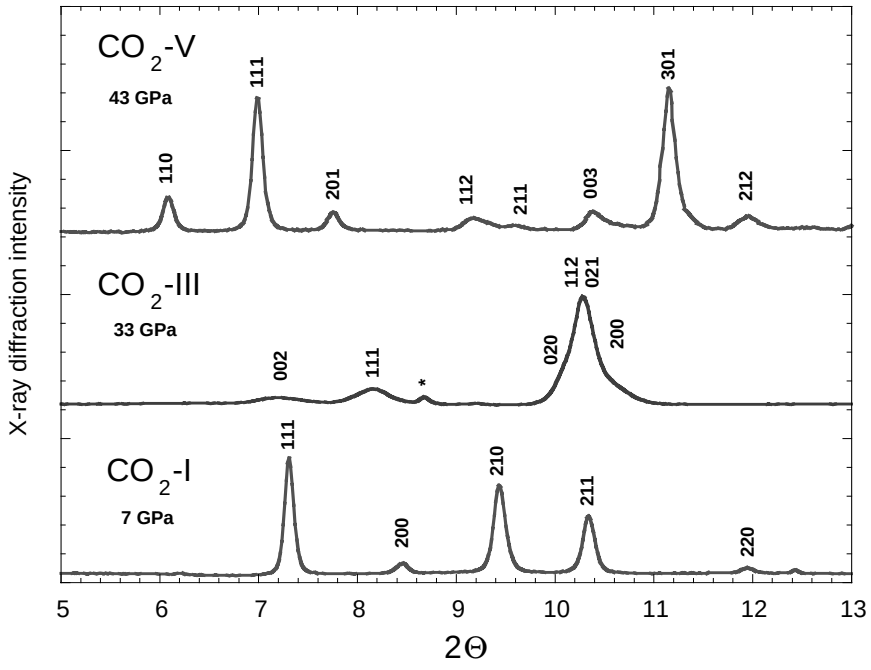

Figure 1. X-ray diffraction patterns of CO_2 phases at high pressures.

In these experiments, the samples were rotated along the chi-direction of the diamond-anvil cell during x-ray exposure, which we found was essential to obtain high quality diffraction pattern from highly preferably oriented CO_2 particularly in the phases III and V. With these results, we were able to characterize the crystal structure of CO_2-V for the first time and the bulk properties of CO_2-I, III and V. Our major findings during this previous run are:

(i) CO_2-III remains in a Cmca structure up to 60 GPa; prior to this study, the crystal structure of CO_2-III had only been determined at the pressures between 8 and 11 GPa, in which conditions CO_2-III always coexists with CO_2-I.

(ii) CO_2-V has indeed a quartz-like ($P6_22$) structure. This is the first example of a tetrahedrally bonded carbon-oxygen structure, which is the basic building block in many covalently bonded solids and minerals including β-SiO_2 quartz.

(iii) CO_2-V is likely a superhard solid similar to cubic-BN; whereas, CO_2-III may not be entirely molecular in its bonding characteristic.

These results will be published in PRL [2].

References:

1. V. Iota, C.S. Yoo, H. Cynn, "Quartz-like CO_2: an optically nonlinear extended solid synthesized at high pressures and temperatures, Science 268, xxx, (1999).
2. C.S. Yoo, H. Cynn, F. Gygi, J. Gali, V. Iota, M. Nicol, S. Carlson, D. Hausermann, L. Yang, C. Mailhiot: "Crystal structures of carbon dioxides at high pressures" submitted to PRL (1999).