

**MS18.02.05 X-RAY DIFFRACTION OF VERY SMALL SAMPLES AT EXTREME CONDITIONS OF PRESSURE AND TEMPERATURE** G. Fiquet, D. Andrault, J.P. Itié, P. Richet, P. Gillet, D. Haüsermann and M. Hanfland, Laboratoire de Sciences de la Terre, ENS Lyon, 46 Allée d'Italie, 69364, Lyon Cedex 07

We present X-ray diffraction measurements carried out at the ESRF at high-pressure and high-temperature in a laser-heated diamond-anvil cell. X-ray diffraction patterns have been recorded up to 28 GPa and temperature in excess of 2500 K in an energy-dispersive mode or with a monochromatic radiation associated with imaging plates. These experiments were conducted on polycrystalline discs or polished thin sections (10-15  $\mu\text{m}$  thick), loaded cryogenically in dry argon acting as pressure transmitting medium, and heated by a CO<sub>2</sub> laser (continuous mode, 120W, TEM 00).

We used an optical set-up designed for the on-line pressure and temperature measurements, where ruby fluorescence and thermal emission of the sample are collected during X-ray diffraction acquisition and directed with optical fibers to a spectrometer placed outside the hutch. In the energy dispersive configuration, exposure times of the order of 300s were long enough to collect diffraction patterns with usable intensities up to 100 keV.

We show results obtained on a CaZrO<sub>3</sub> perovskite compound at high-pressure and high-temperature, which displays an orthorhombic structure at 2980K at 17.5 GPa.

Following these experiments, we present new results obtained with a monochromatic X-ray beam on the ID30-BL27 dedicated high-pressure beamline of the ESRF, realized with a 20X20  $\mu\text{m}^2$  microfocused monochromatic X-ray spot coupled to an *in-situ* area detector.

### High Pressure III Molecules, Ices & Minerals

**MS18.03.01 X-RAY DIFFRACTION STUDY OF PRESSURE-INDUCED POLYMERIZATION IN SIMPLE MOLECULES WITH TRIPLE BONDS.** K. Aoki, H. Yamawaki, M. Sakashita, H. Fujihisa, National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan

Molecules with multibonds often undergo polymerization under pressure. Intramolecular covalent bonding, which is stronger by a factor of several tens than intermolecular bonding, is influenced slightly at modest pressures. However, when molecules are forced to approach beyond threshold distances at sufficiently high pressures, new bonding are formed between adjacent molecules with reconstruction of chemical bonding. Acetylene with a C-C triple bond is one example, which shows successive polymerizations with rehybridization from sp to sp<sup>2</sup> and finally sp<sup>3</sup>. The knowledge of the molecular arrangement at polymerization pressure is essential for understanding reaction mechanism, and hence structural investigation of molecular solid by x-ray diffraction is required.

We have started x-ray diffraction study of simple molecules with triple bonds, which are already found to polymerize under pressure. Attention has carefully been paid for optimization of incident beam intensity and preparation of specimen inside a DAC. Radiation of too much strong x-ray immediately induces polymerization and molecules tend to grow large domains. Preliminary powder diffraction measurement on acetylene with a IP detector gave Debye rings but not sufficiently good for intensity analysis. Mixing of amorphous boron with the specimen is being attempted to prevent particle growth. Besides powder diffraction, we have recently started a single-crystal diffraction measurement with a four-circle device. The results will be presented.

**MS18.03.02 NEW HIGH PRESSURE COMPOUNDS IN METHANE-HYDROGEN MIXTURES.** M. S. Somayazulu, L. W. Finger, R. J. Hemley and H. K. Mao, Geophysical Laboratory and Center for High Pressure Research, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington D.C, 20015.

The effect of chemical interactions in mixtures of molecular systems at high pressures has become the focus of attention recently. Studies on binary molecular systems under high pressure have shown the formation of a variety of van der Waals compounds such as He(N<sub>2</sub>)<sub>11</sub>[1], Ar(H<sub>2</sub>)<sub>2</sub>[2]. A detailed study carried out on the system CH<sub>4</sub>-H<sub>2</sub> using a combination of single crystal x-ray diffraction, Raman scattering and IR spectroscopy has shown the existence of four new compounds (CH<sub>4</sub>)<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>(H<sub>2</sub>)<sub>4</sub>, CH<sub>4</sub>(H<sub>2</sub>)<sub>2</sub> and CH<sub>4</sub>H<sub>2</sub> in this system[3]. Of these, (CH<sub>4</sub>)<sub>2</sub>H<sub>2</sub> and CH<sub>4</sub>H<sub>2</sub> are found to be stable to pressures of the order of 60 GPa. In addition, it was also possible to crystallize pure methane in a quasi-hydrostatic medium of (CH<sub>4</sub>)<sub>2</sub>H<sub>2</sub>. Single crystal diffraction of methane to pressures of the order of 15 GPa were thus possible. The talk will summarize the phase diagram of this binary system, the structural details of the molecular compounds formed and also discuss the recent results on the structural transitions in pure methane.

[1] W. L. Vos, L. W. Finger, R. J. Hemley, J. Z. Hu, H. K. Mao and J. A. Schouten, Nature 358 (1992) 46-48.

[2] P. Loubeyre, R. LeToullec and J.-P. Pinceaux, Phys. Rev. Lett. 72 (1994) 1360.

[3] M. S. Somayazulu, L. W. Finger, R. J. Hemley and H. K. Mao, Science (in press) (1996)

**MS18.03.03 HOST STRUCTURE AND GUEST OCCUPANCY OF N<sub>2</sub>-AND O<sub>2</sub>-CLATHRATES AS A FUNCTION OF PRESSURE BY NEUTRON POWDER DIFFRACTION.** W. F. Kuhs\*, B. Chazallon\*, F. Pauer\*\*, \*Mineralogisch-Kristallographisches Institut, Universität Göttingen, Goldschmidtstr.1, D-37077 Göttingen, \*\*Alfred-Wegener-Institut für Polar- und Meeresforschung, Columbusstraße, D-27568 Bremerhaven

Air-clathrates crystallize (at least at lower pressures) in the Stackelberg type II clathrate structure as do the pure O<sub>2</sub>- and N<sub>2</sub>-clathrates and they occur naturally in deeper parts of the arctic and antarctic ice shields. In order to elucidate the thermodynamic and structural properties of natural air-clathrates we have synthesized the pure N<sub>2</sub>- and O<sub>2</sub>-clathrates and analyzed their structure and composition by neutron diffraction in the range of 150 to 2500 bar nitrogen and 120 to 330 bar oxygen pressure respectively. The main question is whether or not the filling follows a Langmuir isotherm corresponding to an ideal solid solution behaviour and how important the differences are between the nitrogen and the oxygen filling at given pressures in the pure phases. Diffraction is the appropriate technique allowing for the determination of the filling behaviour vs. gas pressure (fugacity) for the different types of cages in the clathrate structure (which is not possible with standard physicochemical studies); neutron diffraction permits *in-situ* work under high gas pressures. The experiments were performed at the Institute Laue-Langevin in Grenoble with high pressure cells developed by us for the use in standard "orange" cryostats.

We will give details of the sample preparation and the results of the crystal structure refinements by Rietveld refinement techniques for a variety of samples at different pressures and temperatures, and as a function of reaction time. We have determined the degree of filling for the small and large cages as a function of pressure. For the first time we have evidence for a double occupancy of the large cages, a fact which up to now has not been considered in theoretical calculations of the clathrate filling behaviour. We also have observed the (already predicted) occurrence of a Stackelberg type I clathrate at higher gas pressures as well as their back-transformation to a type II structure on cooling. Finally the relevance of these results for the work on air-clathrate inclusions in ice cores will be discussed.