

## 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://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

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.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal 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.



	<b>Experiment title:</b> Physics and Chemistry of Simple Molecules, Nano-confined at High Pressures in 1D, all SiO <sub>2</sub> Zeolites: a Powder XRD Investigation.	<b>Experiment number:</b> <b>CH-4538</b>
<b>Beamline:</b> ID09A	<b>Date of experiment:</b> from: 10/10/2015 to: 13/10/2015	<b>Date of report:</b> 16/05/2016
<b>Shifts:</b> 9	<b>Local contact(s):</b> Gaston Garbarino	<i>Received at ESRF:</i>

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## Report:

### Scientific background :

We have recently shown that simple molecules such as Ar, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> can be efficiently packed in the nano-channels of silicalite [1-5] at 0.1-20 GPa using diamond anvil cells (DACs). A pure SiO<sub>2</sub> zeolite was chosen to avoid catalysis and study the sole effect of pressure on pore filling and polymerization in the case of the hydrocarbons. Nano-composites of polyethylene(acetylene)/silicalite were obtained by these mechanochemical approaches and recovered at room pressure [4, 5]. These composites exhibit interesting physical properties. Their compressibility is strongly reduced and the thermal expansion changes from negative to positive. Structural studies of confined molecular systems have been limited so far to the samples recovered at room P using laboratory diffractometers and to the silicalite as the host zeolite material, which is a 3D channel system.

The aim of the present experiment was to perform synchrotron, powder XRD studies on three guest systems confined this time in a 1D channel zeolite, TON, at 0.1-20 GPa: Ar, Ne and CO. Insertion of the two noble gases in the 1-D zeolite provides model systems for pore filling allowing for the investigation of potential ordering and eventual commensurate host-guest arrangements. The structural study of the polymeric CO (pCO) filled zeolite show how this normally unstable polymer is arranged in a protective 1-D host zeolite system. This material, which, in addition to modified mechanical properties, could present interesting electrical and optical properties due the presence of conjugated chains. The room P recovered polyCO/TON composite is also of great interest as an energetic material.

### Experimental procedure:

Membrane diamond anvil cells (MDAC) equipped with stainless steel gaskets were used for the studies of Ne and Ar insertion and the polymerization of confined CO in TON, i.e. for the synthesis of pCO/TON. Typical sample dimensions were 100–300 μm in diameter and 40–50 μm in thickness. Ar and carbon monoxide were

loaded cryogenically in the liquid phase at 1-2 bar and 77 K, together with the powdered TON. Ne was loaded at high pressure using the Sanchez Technologies gas loading system at the ESRF. A ruby chip was also put in the sample chamber for pressure measurements. Synchrotron XRD was performed on the ID09A beamline of the ESRF with a monochromatic beam ( $\lambda=0.414132 \text{ \AA}$ ) and a MAR555 flat panel detector. The nominal size of the focal spot was 20  $\mu\text{m}$ . The diffraction patterns were analyzed and integrated using the FIT2D program. The Rietveld refinements were performed with the program Fullprof.

### **Preliminary Results:**

Data analysis is still in progress. Preliminary Rietveld refinements of the crystal structure of TON indicate that 4 Ne atoms enter the unit cell of TON completely filling the pores. The high values of the atomic displacement parameters indicate that the neon atoms are highly disordered. The compressibility and structural distortions at high pressure are considerably reduced as compared to the empty-pore TON zeolite. In addition, the crystalline form persists to pressures of the order of 20 GPa and is recovered after decompression. The results show the very strong effect of pore filling by a noble gas on the structural stability and mechanical properties of this 1-D zeolite-type material. Analysis of the data in Ar is in progress, but is more difficult due to the solidification of Ar just above 1 GPa inducing non-hydrostatic stress and contamination of the diffraction pattern due to strong scattering from solid Ar.

The structure of the polyCO/TON nanocomposite was determined using data obtained on the sample recovered in the gasket after high pressure treatment at 7 GPa. Difference Fourier maps were used to locate the atoms in the polymer chains and the structure of the guest polymer/ host zeolite system was refined by the Rietveld method, Fig. 1. About 2.5 CO units were present in each unit cell corresponding to filling of 25% of the pores. The tight spatial constraints in the  $4.6\text{\AA}\times 5.7\text{\AA}$  pores of the TON zeolite lead to a more ordered polymer than observed in the bulk. This material is also stable after pressure release in contrast to the bulk polymer, which reacts with atmospheric  $\text{H}_2\text{O}$ . Nanoconfinement thus appears to be a way to stabilize this potential energetic material.

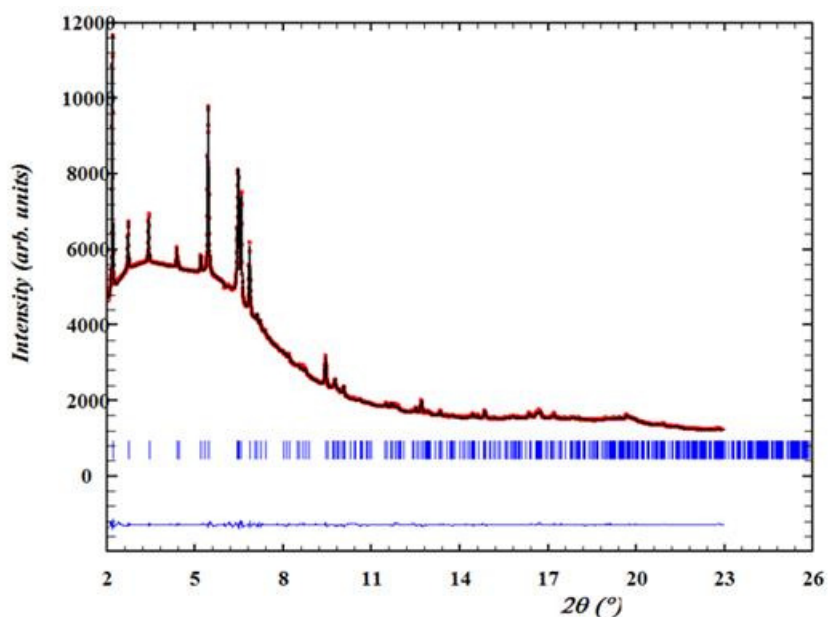


Fig. 1. Experimental, calculated and difference profiles from the Rietveld refinement of the polyCO/TON nanocomposite.

### **References**

- [1] J. Haines, et al., *J. Am. Chem. Soc.* **132**, 8860 (2010).
- [2] M. Santoro, et al., *Proc. Natl. Acad. Sci. U.S.A.* **108**, 7689 (2011).
- [3] M. Santoro, et al., *Nature Communications* **5**, 3761 (2014). DOI: 10.1038/ncomms4761.
- [4] M. Santoro, et al., *Nature Commun.* **4**, 1557 (2013) doi:10.1038/ncomms2564.
- [5] D. Scelta, et al., *Chem. Mater.* **26**, 2249-2255 (2014).