ESRF	**Experiment title:** Nano-Extreme :Extreme conditions of pressure and temperature for the elaboration of new carbon based nano-materials	**Experiment number**: CH-1704
Beamline:	**Date of experiment**: from: 07 April 2004 to: 13 April 2004	**Date of report**: *Received at ESRF:*
Shifts:	**Local contact(s)**: O. Mathon / S. Pascarelli	

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Report:

This proposal was awarded with a *Medium Term Project* (2004/I and 2004/II: 2 * 15 shifts) with the possibility of extension to a long term project after review.
We will present the results distributed in the 3 periods of the project, corresponding to the obtained results in conditions of increasing technical difficulties:

a) High pressure experiments up to 15 GP at ambient temperature.
b) High pressure experiments up to 15 GPa at high temperature
c) HP-HT experiments in anaerobic conditions.

During this project, different set-ups have been tested in the Paris-Edinburgh cell, including:
- 5 mm sintered diamond anvils.
- a totally new cell including Rh resistive heating with windows for the X-ray path.
- a clamp system for the cell loading in the glove-box
- a cooling system adapted to work together with the clamp system.

We have gained considerable progress in the technical part of the project. We have for the first time been able to acquire **high quality classic EXAFS** data at pressures of **15 GPa and temperatures of 1500 °C**. This corresponds to double the pressure domain attainable in such experiments with respect to what has been previously achieved at the ESRF. It was part of this project to make this technology available to ESRF users, in collaboration with the ESRF EXAFS group: this in fact has been achieved and the project can be considered successful.

Part I : High pressure studies at ambient temperature

Two families of compounds were studied up to 14 GPa at ambient temperature: doped silicon clathrates and doped Single-Wall Nanotubes (SWNT).

First, Paris-Edinburgh V4 Press (up to 14 GPa) and Diamond Anvil Cell (up to 49 GPa) techniques were associated to explore pressure-induced transitions in silicon clathrates, combining x-ray absorption and

x-ray diffraction. Ba_8Si_{46} clathrate at the Ba K-edge up to 14 GPa (Fig 1) and Rb_6Si_{46} up to 12 GPa at the Rb K-edge have been studied.

Very high quality data were obtained. The results on Ba_8Si_{46} have been published in two separate papers (Please find attached abstracts below) and have been presented at the SRMS-4 International congress (Grenoble, 23-25 august) in an oral contribution.

Results for Rb_6Si_{46} are currently being prepared for publications.

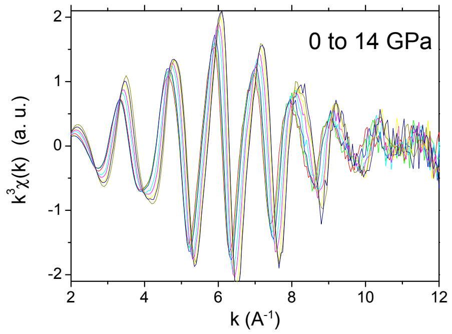
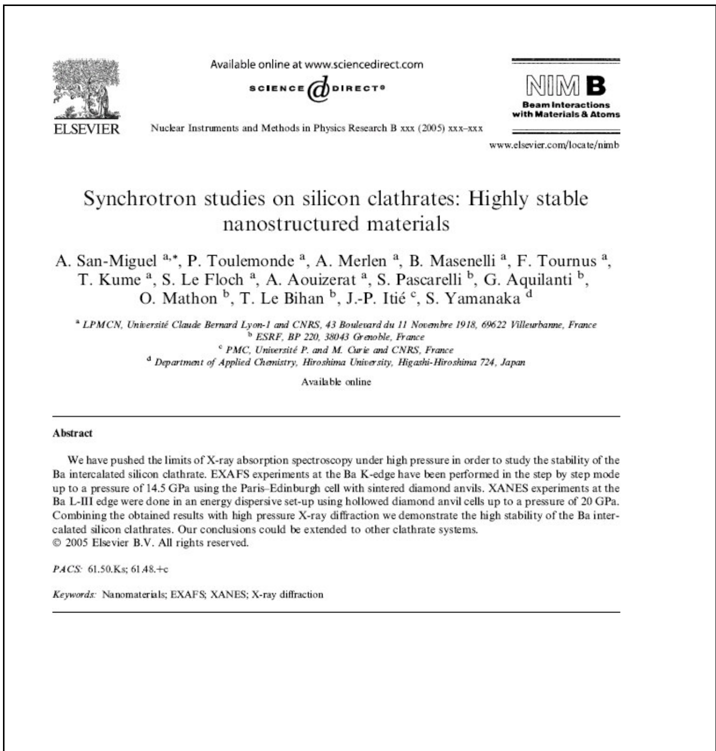


Figure 1. ***Ba K-edge EXAFS of Ba_8Si_{46} from ambient pressure to 14 GPa. The data show that the Ba atoms remain at the centre of the Si nano-cages up to that pressure contrarily to what has been proposed (T. Kume et al., Phys Rev Lett, 2003)***



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Synchrotron studies on silicon clathrates: Highly stable nanostructured materials

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Available online

Abstract

We have pushed the limits of X-ray absorption spectroscopy under high pressure in order to study the stability of the Ba intercalated silicon clathrate. EXAFS experiments at the Ba K-edge have been performed in the step by step mode up to a pressure of 14.5 GPa using the Paris–Edinburgh cell with sintered diamond anvils. XANES experiments at the Ba L-III edge were done in an energy dispersive set-up using hollowed diamond anvil cells up to a pressure of 20 GPa. Combining the obtained results with high pressure X-ray diffraction we demonstrate the high stability of the Ba intercalated silicon clathrates. Our conclusions could be extended to other clathrate systems.

PACS: 61.50.Ks; 61.48.+c

Keywords: Nanomaterials; EXAFS; XANES; X-ray diffraction

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Pressure-induced homothetic volume collapse in silicon clathrates

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PACS. 61.50.Ks – Crystallographic aspects of phase transformations; pressure effects.
PACS. 61.48.+c – Fullerenes and fullerene-related materials.

Abstract. – The high-pressure properties of the Ba-doped silicon clathrate Ba_8Si_{46} have been investigated combining X-ray diffraction and X-ray absorption spectroscopy. A pressure-induced isostructural phase transition associated with an important volume collapse takes place at 11.5–14 GPa. This transformation is characterized by the homothetic contraction of the silicon cages containing the Ba atoms. This transition is preceded by a change in the electronic structure at 5 GPa in good agreement with Raman spectroscopy observations (T. Kume *et al.*, *Phys. Rev. Lett.*, **90** (2003) 155503) that it is also of isostructural nature. The cage structure is preserved through the phase transitions allowing to obtain tetrahedral silicon with record interatomic distances as low as 2.13 Å. At the highest studied pressure of 49 GPa, the structure becomes irreversibly amorphous. The physical origin of the homothetic isostructural transitions is discussed.

The second set of experiments on intercalated SWNT was carried in order to understand the role of the guest atoms as a "structure dirigent agent" in the high pressure routine.

Iodine intercalated SWNT has the advantage of being one of the few simple carbon intercalated compounds interesting to our project that can be manipulated in air. We performed this experiment at the iodine K-edge.

The sample was primarily washed with alcohol to remove the iodine I_2 in excess. We performed **x-ray absorption** for oil pressure up to 340 bars. Simultaneously, using the x-ray detector (MAR), it was possible to get the **x-ray diffraction** of the sample. XRD data were also used to obtain *in situ* pressure measurements monitoring changes in the *d*-spacing of a pressure marker (h-BN). Pressure has been estimated using the Birch-Murnaghan equation of state. In the EXAFS pattern (fig.2) we observe a change in the oscillations between 5 and 8 GPa. No additional transition was observed at higher pressure. EXAFS spectra before and after high pressure cycle are almost identical indicating that the transition is certainly reversible.

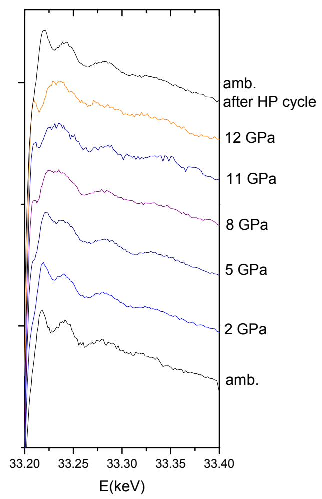

Figure 2 : ***I K-edge EXAFS of washed Iodine doped SWNT from ambient pressure to 12 GPa.***

These results are part of the PhD thesis of A. Merlen (U. Lyon-1) and are submitted for publication