



	<b>Experiment title:</b> <b>Origin of the cage collapse transformation in silicon clathrates</b>	<b>Experiment number:</b> HS 2259
<b>Beamline:</b>	<b>Date of experiment:</b> from: 08 October 2003 to :15 October 2003	<b>Date of report:</b> 31/08/2006
<b>Shifts:</b>	<b>Local contact(s):</b> Sakura Pascarelli	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants:</b> A. SAN MIGUEL, P. TOULEMONDE, A. AOUIZERAT, A. MERLEN Laboratoire de Physique de la Matière Condensée et Nanostructures <b>Université Lyon 1 and CNRS, France</b>		

## Report:

EUROPHYSICS LETTERS

15 February 2005

*Europhys. Lett.*, **69** (4), pp. 556–562 (2005)

DOI: 10.1209/epl/12004-10387-x

### Pressure-induced homothetic volume collapse in silicon clathrates

A. SAN MIGUEL<sup>1</sup>(\*), A. MERLEN<sup>1</sup>, P. TOULEMONDE<sup>1</sup>, T. KUME<sup>1</sup>(\*\*),  
S. LE FLOCH<sup>1</sup>, A. AOUIZERAT<sup>1</sup>, S. PASCARELLI<sup>2</sup>, G. AQUILANTI<sup>2</sup>,  
O. MATHON<sup>2</sup>, T. LE BIHAN<sup>2</sup>, J.-P. ITIÉ<sup>3</sup> and S. YAMANAKA<sup>4</sup>

<sup>1</sup> *Laboratoire de Physique de la Matière Condensée et Nanostructures  
Université Claude Bernard Lyon-1 and CNRS - 43 Bd. du 11 Novembre 1918  
69622 Villeurbanne, France*

<sup>2</sup> *European Synchrotron Radiation Facility - BP 220, 38043 Grenoble, France*

<sup>3</sup> *Physique des Milieux Condensés, Université P. and M. Curie and CNRS - France*

<sup>4</sup> *Department of Applied Chemistry, Faculty of Engineering, Hiroshima University  
Higashi-Hiroshima 724, Japan*

received 24 September 2004; accepted in final form 10 December 2004

published online 21 January 2005

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<sub>8</sub>Si<sub>46</sub> 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.



## Synchrotron studies on silicon clathrates: Highly stable nanostructured materials

A. San-Miguel <sup>a,\*</sup>, P. Toulemonde <sup>a</sup>, A. Merlen <sup>a</sup>, B. Masenelli <sup>a</sup>, F. Tournus <sup>a</sup>,  
T. Kume <sup>a</sup>, S. Le Floch <sup>a</sup>, A. Aouizerat <sup>a</sup>, S. Pascarelli <sup>b</sup>, G. Aquilanti <sup>b</sup>,  
O. Mathon <sup>b</sup>, T. Le Bihan <sup>b</sup>, J.-P. Itié <sup>c</sup>, S. Yamanaka <sup>d</sup>

<sup>a</sup> LPM CN, Université Claude Bernard Lyon-1 and CNRS, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne, France

<sup>b</sup> ESRF, BP 220, 38043 Grenoble, France

<sup>c</sup> PMC, Université P. and M. Curie and CNRS, France

<sup>d</sup> Department of Applied Chemistry, Hiroshima University, Higashi-Hiroshima 724, Japan

Available online 1 August 2005

### 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.

© 2005 Elsevier B.V. All rights reserved.

PACS: 61.50.Ks; 61.48.+c

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