Silicon clathrates under high pressure conditions

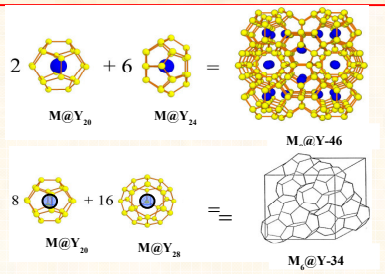
A. San Miguel, P. Toulemonde, X. Blase, S. Le Floch, A. Merlen
LPMCNanostructures, Université Lyon 1 et CNRS, France
S. Pascarelli, G. Aquilanti, O. Mathon, T. Le Bihan
ESRF, Grenoble, France
email : sanmigue@lpmcn.univ-lyon1.fr

Introduction.

Building blocks :
Nano-cages associated in 4-fold coordinated in sp^3 bonding configurations

Y = C(?), Si, Ge, Sn

M= Na, K, Rb, Ba, Sr, I,…



First synthesis :
ICMCB, Bordeaux, J.S. Kasper, P. Hagenmuller, M. Pouchard, C. Cros, 1965.

Superconductivity :
T_c = 8 K in Ba_8Si_{46}

Large gap semiconductor :
Eg = 1.9 eV in Si-34 (Si_{136})

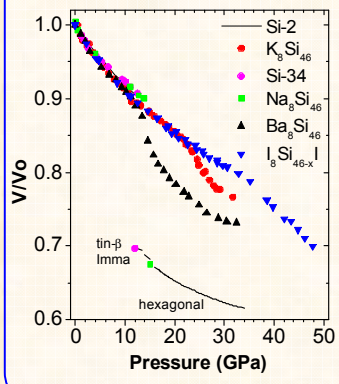
Thermoelectric properties :
PGEC (Phonon Glass Electron Crystal)

Stability and cohesivity
The subject of this poster

Conclusions

- Group IV clathrates are extremely **stable and cohesive** materials, particularly with convenient intercalation.
- Carbon clathrates : candidates to combine **outstanding mechanical properties** and tailored electrical characteristic through intercalation.
- High Z-intercalated clathrates : new type of **isostructural and homothetic** phase transitions with extreme volume collapse

Outstanding Stability of Si intercalated clathrates

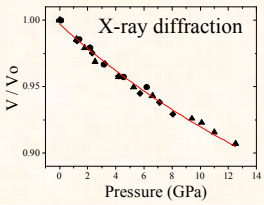


Clathrate	Transition type	Transition pressure (GPa)
Si-34	1st order	11.5
Na_8Si_{46}	1st order	11.5
Ba_8Si_{46}	2nd order	11.5 (amorphisation ~ 45 GPa)
K_8Si_{46}	2nd order	25
I_8Si_{46}	2nd order	35

• Up to x3 the one of silicon diamond

Extraordinary mechanical properties

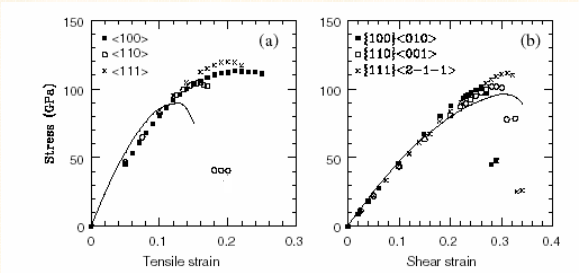
• Low compressibility of empty clathrates



Bo (GPa)	Measured	Calculated
Si-2	97	96.7
Si-34	90	87.7
C-2	446	462
C-34	-	398

A. San Miguel, P. Mélinon, X. Blase et al., Phys. Rev. Lett. **83** (1999)

• Exceptional ideal strength of C-clathrates



X. Blase, P. Gillet, A. San Miguel and P. Mélinon, Phys. Rev. Lett. **92** (2004)

• Improved compressibility by intercalation

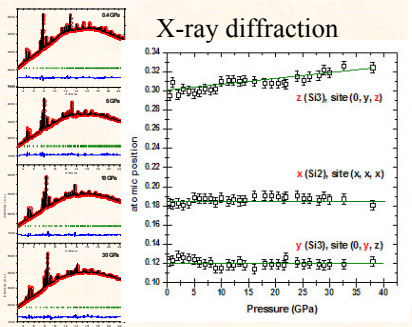
	B_o exp. (GPa)	B_o calc. (GPa)	$B_o$calc –B_o(Si-2) (%)
Xe_8Si-46	N.S.	85	12
Si-46	N.S.	87	10
Si-34	90±5	87.5	9.5
Ba_8Si-46	93 ±5	-	-
I_8Si-46	95±5	91	6
Te_8Si-46	N.S.	95	2
Sn_8Si-46	N.S.	96	1
Si-2 diamond)	97.88	97	0

A. San Miguel, P. Mélinon, X. Blase et al., Phys. Rev. B. **65** (2002)

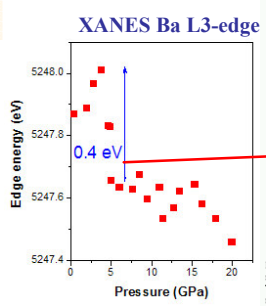
A new type of homothetic isostructural transition in Ba_8Si_{46}

A. San Miguel, , A. Merlen, P. Toulemonde, T. Kume, S. Le Floch et al. **Europhysics Lett**, , 69, issue #4, 15 February 2005

•No pressure evolution of the Si atomic positions



•Change of hybridization at 5-7 GPa



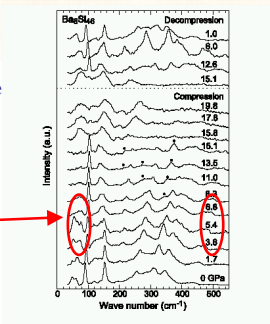
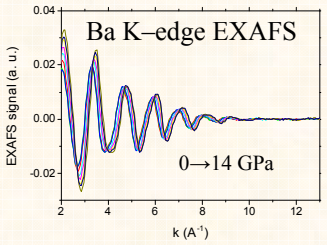


FIG. 2. Pressure dependence of Raman spectra of Ba_8Si_{46}, measured on the compression and decompression processes. The maximum pressure was 19.8 GPa in the present experiments. Solid circles indicate new peaks concerned with the phase transition at 7 GPa.

Raman data : *T. Kume et al.* PRL **90** 155503 (2003).

• No displacement of Ba atoms



• Up to 30% homothetic volume reduction