A NEW CLASS OF LOW COMPRESSIBILITY MATERIALS: CLATHRATES OF SILICON AND RELATED MATERIALS

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We discuss the high pressure properties of different silicon clathrate structures that we have investigated by means of X-ray diffraction and *ab initio* calculations. Compressibility, transition pressures or phase transformations are interpreted as a function of the nature of the guest atom intercalation. The compressibility of the clathrate structure is in all cases close to that of silicon diamond whereas transition pressures or the high pressure phases are extremely depending on the nature of the guest atom. We address the implications for obtaining a metallic material as hard as diamond.

Silicon clathrates, called also enclosure or cage compounds are crystalline assemblages of face sharing low order (20, 24, 28 atoms) fullerene type units (Fig. 1). Charged clathrates are intercalated-type compounds in which the host-guest interaction are fundamental in the synthesis process. In fact the guest atom or molecule acts as a steric barrier conforming the cage-structure of the host and for this reason these guests are also called "structure directing agents". The nature of the guest-host interaction is fundamental to define the properties of the clathrate system.

Different properties of group-IV clathrates are driving much attention because of possible applications: superconductivity [1], thermoelectric applications [2], magnetic materials [3] or wide band gap semiconductors [4]. In addition, we have recently shown [5, 6] that carbon-clathrates, if synthesized are good candidates to bring new hopes in the world of superhard materials.

Clathrate structures of type I or II are essentially found in three different families of compounds: ice clathrates that were the first to be discovered, SiO_2 clathrates or clathrasils and column IV (Si, Ge, Sn) clathrates. Natural forms are found for the two first types whereas clathrates of silicon and related materials were for the first time synthesized about thirty
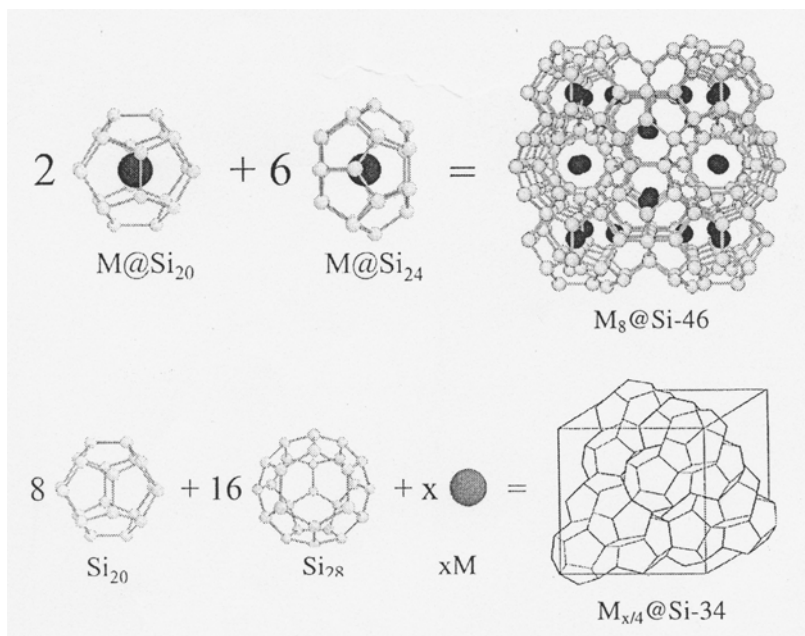
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FIGURE 1   Silicon clathrates are cubic 3-D arrangements of sp^3 tetrahedral units of (a) Si_{20} and Si_{24} cages (type-I, noted Si-46 or Si_{46}) (b) Si_{20} and Si_{28} cages (type-II, noted Si-34 or Si_{136}). Their topology allows the introduction of guest atoms (M) in the cages ($M_x@$Si-46 for instance with all cages full when $x = 8$).

five years ago [7]. Both type I and II clathrates are cubic structures, respectively noted for the silicon case, $M_x@$Si-46 (simple cubic) and $M_x@$Si-34 (fcc) where M denotes the guest atom. The stoichiometry of the Bravais lattice is also used in clathrate notation giving respectively M_xSi_{46} and $M_{4x}Si_{136}$ for type I and II. Intriguingly enough, the case $x \approx 0$ is only known for Si-34 for which the structure directing agent (Na) is evacuated by pumping under heating. An essential feature of silicon clathrates is the *quasi sp^3* character of the silicon bonding. In fact all silicon atoms are 4-fold coordinated with angles and distances close to the ones of the silicon diamond structure. On the other side, the special clathrate architecture gives rise to an open structure with a strong dominance of pentagonal rings (up to 87% in type II clathrates) originated by the eclipsed network of the Si-tetrahedra. Synthesis of carbon clathrates of the type I and II has not been yet reported, even if total energy calculations indicate that the structure will be only slightly metastable with respect to the diamond structure [8]. An empty silicon clathrate can then be considered as having a local structure and bonding close to the silicon diamond one. Nevertheless because of the excluded volume in the cages, it is an expanded structure with an atomic volume approximately 11% greater than its diamond analog. Si-34 is also a semiconductor, but having a gap as large as 1.9 eV.

We have studied the cohesive and stability properties of the empty type-II clathrate Si-34 and of different fully intercalated type-I silicon clathrates (M = Na, Ba, I) both through X-ray diffraction experiments and *ab initio* calculations within the density functional theory (DFT). Energy dispersive X-ray diffraction experiments were performed at the DW11 station of LURE (Orsay, France). Fine grained powder samples were loaded in diamond anvil cells using different pressure transmitting media and taking special care in avoiding grain bridging effects. The linear ruby fluorescence shift was used for the pressure calibration. Both experiments and calculations let us conclude that the non-doped Si-34 clathrate has a highly stable structure with a bulk modulus very close to the Si-diamond one [5]. In fact no phase transi-

tion was found before 11.5 GPa were Si-34 transforms to the β-tin phase and continuous following the normal high pressure phase diagram of silicon at high pressure. This phase transformations exhibits a tremendous volume collapse of 33% and it is not clear to us if such transformation can be of the martensitic type or if a fully reconstructive transformation must be considered.

The high value of the bulk modulus of Si-34 immediately calls for an analogy in the carbon case. In fact, we have shown from calculations [5], that C-34 will be a low compressibility material (see Tab. I). Low compressibility, even if generally encountered in super-hard materials, is not the best criteria for hardness. Nevertheless, other clues indicate that carbon clathrates (C-34 or C-46) would exhibit high hardness. First, the silicate analogue of the type I silicon clathrates, a mineral called melanophlogite [$Si_{46}O_{92}$] exhibits values of Vickers hardness between 6.5 and 7, that are, close to 7 of quartz. On the other side, recent semi-empirical calculations [8] indicate that the hardness of C_{46} could be one of the highest after the diamond one. Also, we can find analogies between group-IV clathrates and the high pressure 3D-polymerized fullerenes that have already shown super-hard behavior [9]. Nevertheless, a possible synthesis of carbon clathrates will probably be mediated by "structure directing agents" as Li or Na, and the effect of intercalation in the cohesion properties should be also studied. As a general approach we can attempt to divide the effect of clathrate intercalation in two terms: (i) the size effect of the guest atom and (ii) the effect of host-guest electronic interaction. These two effects can differently affect the compressibility of the solid. For large size guest atoms, an excluded volume effect gives rise to an expanded network, and we can expect a reduction of the value of the bulk modulus. We have in fact verified this point [6] by *ab initio* DFT-LDA calculations in the case of Xe_8Si_{46}, that should exhibit a negligible guest-host interaction (see Tab. I). We have found that this hypothetical clathrate would have a bulk modulus 12% smaller than the one of the Si_{46} empty clathrate.

Table I summarizes the obtained values for the bulk modulus of different clathrates structures obtained experimentally or through calculations. We firstly observe that with the exception of the already mentioned Xe intercalated clathrate, all the other intercalated clathrates have higher values of the bulk modulus than the empty ones. This evidences that the guest-host interaction can compensate for volume exclusion effects of the guest atom and even decrease the compressibility of the clathrate network to values equivalent to the one of the diamond structure. It is interesting to note that Sn_8Si_{46} can be shown on the basis of band structure calculations [10] to be strongly metallic with the Fermi level located in a peak of the density of states. These results lend support to the idea that compounds as Li_8C_{46} or Na_8C_{46} could constitute candidates for new metallic super-hard materials.

TABLE I Experimental and *ab initio* Calculated Bulk Modulus of Silicon Clathrates and their Comparison with the Diamond Structure.

	Bo (GPa)		Bo(Si-2)-Bo (%)	
	Exp	*Calc*	*Exp*	*Calc*
Xe_8Si_{46}	Not synth	85	–	12
Si_{46}	Not synth	87/83	–	10
Si_{136} (or Si-34)	90	87.5	8	9.5
Ba_8Si_{46}	93 ± 5	–	5	–
I_8Si_{46}	95 ± 5	91	3	6
Te_8Si_{46}	Not synth	95	–	2
Sn_8Si_{46}	Not synth	96	–	0
Si-2 (diamond)	97.88	97	–	0

Let us now consider the pressure stability of silicon clathrates. There has been a limited number of investigation on water or clathrasils at high pressure. Clathrasils (dodecasil-3C and dodecasil-3R) reversibly amorphizase under high pressure [11] whereas methane hydrate clathrate destabilizes at 1.2 GPa but maintaining the hydrated character at least up to 9 GPa [12]. We have found that all the studied silicon clathrates remain stable up to pressures equal or higher than the one of the diamond structure of silicon. The structure of all studied silicon clathrates destabilize when the Si-Si mean distance attains a value of 2.30 Å independently of the clathrate type and of their high pressure structure [6]. This result is even applicable to the non-hydrostatically compressed Si in the diamond structure. We should recall that the clathrate structure is made of distorted Si tetrahedra as would be expected for non-hydrostatic silicon in the diamond structure. The domain of pressure for these phase transitions extends from 7 GPa for stressed Si-2 up to 17 GPa for I_8Si_{46}. For all type I clathrates, the observed instability corresponds to the same value of the host structure cell parameter. It has been recently suggested [13] that in the case of K_8Si_{46}, its phase transformation will be due to the presence of a phonon instability of acoustic modes. Silicon clathrates are phonon glass crystals, where the lattice dynamics is dominated by host dynamics. Consequently, this phonon instability should be generalized to other clathrate structures having the same cell parameter, and explaining the observed instability of type I clathrates. It is not clear whether or not these speculations can be extended to explain the instability of type II clathrates or even the one of stressed Si-diamond.

We consider now the structure of intercalated silicon clathrates after the instability. Two different types of behavior are observed. For Na [6], K [14] and for the empty clathrate [5], the high pressure structure is the corresponding high pressure structure of silicon at the transition pressure of the clathrate. These phases are simple hexagonal for the Na and K clathrate and of the β-tin type for Si-34. For the Ba and I intercalated clathrate, we observe a totally different behavior [6]. There is a volume collapse of the clathrate structure, without involving a change of symmetry. In the Ba clathrate this collapse takes place continuously with a 8.8% volume reduction in a pressure domain of 4 GPa (from the onset of the collapse at 13.2 GPa). On the contrary, in the iodine clathrate we only observe a small volume reduction of 1–2% at 17 GPa. In both cases, the clathrate diffraction peaks can be followed without the appearance of new peaks up to the highest pressure studied of 35 GPa. In Ba_8Si_{46}, the progressive widening of the diffraction peaks and the progressive disappearance of the less intense ones, can be considered as signs of a possible pressure induced amorphization. The recovered sample after quench from that pressure was in fact amorphous.

We can be tempted to invoke some kind of steric barrier effect to explain the two different types of behavior after the clathrate instability. Table II shows the atomic volume of alkali atoms and Ba at the two extreme pressures (11.5 and 17 GPa) where phase transformations of silicon clathrates have been observed. As the Ba value is in between the Na and K ones, we have to conclude that hybridization processes must be taken into account to understand the high pressure behavior after the instability. This should be put in relation with the fact that superconductivity in Si clathrates is associated to the presence of Ba [1]. In the iodine case, where we only observe a very weak instability, DFT-LDA calculations conclude [10] on an iono-covalent guest-host interaction, but the differences in the electronic structure of iodine and other guest atoms do not allow to make a clear parallel.

It is interesting to compare the compressibility of the barium clathrate with the one of the elemental Ba. In Figure 2 it is shown the measured atomic volume of elemental Ba [15] (that follows two consecutive phase transitions in this pressure domain) together with the one of Si-2 and of Ba_8Si_{46}. The atomic volume of Ba_8Si_{46} has been calculated as $a^3/54$, with "a" equal to the cell parameter. We have scaled the atomic volume of Ba by a factor 0.59 to match the atomic volume of Ba_8Si_{46} at the pressure instability (13 GPa). We observe that up to this

TABLE II   Atomic Volume of Elements (that can be Intercalated in Clathrates) at the Two Extreme Pressures where the Instability of the Silicon Clathrate Structure has been Observed.

	V_{atom} ($Å^3$) at 11.5 GPa	V_{atom} ($Å^3$) at 17.0 GPa
Li[a]	13.9	12.2
Na[b]	21.9	19.4
K[c]	37.1	32.2
Rb[d]	35.5	27.5
Cs[e]	31.2	28.9
Ba[f]	32.4	28.6

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[f]R. J. Nelmes *et al.* (1999) *Phys. Rev. Lett.* **83**, 4081.

instability the compressibility of Ba_8Si_{46} is comparable with the one of Si-2 whereas from that pressure, it compares remarkably well with the one of atomic barium. At higher pressures, where signs of a possible amorphization appear, the agreement is less pronounced. We obtain the image of a host-mediated compressibility before 13 GPa and of a guest-driven one for higher pressures. This will imply that from 13 GPa, the compressibility is dominated via the Ba-host cage interaction and that the repulsive part of this interaction is closely related to the Ba-Ba one of the barium IV self-hosting incommensurate structure (or of a high compact structure in general). Further research is in course to understand these observations.

In conclusion, we have shown that silicon clathrates, in spite of their relatively simple 3D cage-based structure exhibit a rich variety of pressure behavior. We have demonstrated that, prior to the clathrate instability, the cohesion and stability of silicon clathrates is essentially host controlled. Actually, we have seen that the compressibility of the clathrate, already close
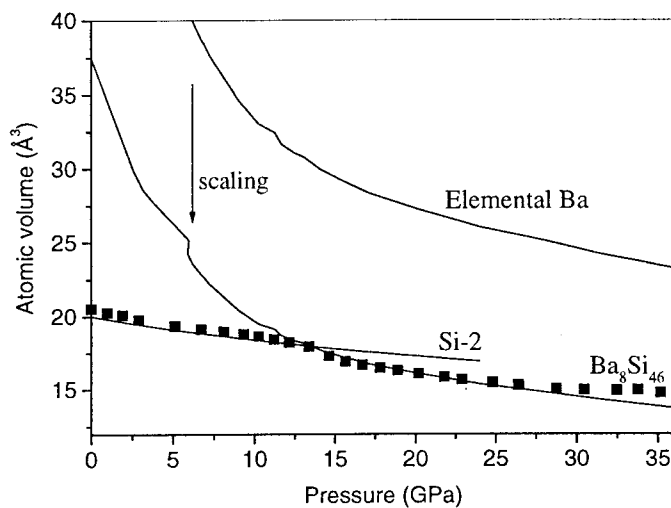

FIGURE 2   Comparison between the evolution of the atomic volume in Ba_8Si_{46} (squares), Si-2 and elemental Ba. This last one is also shown scaled by a factor 0.59 to match the atomic volume of Ba_8Si_{46} at the pressure instability (13 GPa).

to the one of the diamond structure, is maintained or even slightly enhanced by convenient intercalation. In this region prior to the instability, the cohesion and stability effect of the guest element is limited to: (a) modify the ambient value of the clathrate cell parameter, which will determine the transition pressure b) introduce a guest-host hybridization that can slightly modify the compressibility (up to 10–15% from our calculations). After the phase transition we observe in contrast a strong dependence of the structural evolution on the type of guest atom. With iodine guests the clathrate continues to reduce its volume practically as before the instability, barium guests seem to block a phase transformation but cannot avoid a volume collapse and amorphization [16], whereas Na or K do not seem to alter much the silicon physics and a phase transformation with 1/3 volume reduction. Finally, we have noted that intercalated carbon clathrates provide some hope for obtaining a metal almost as hard as diamond.

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