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# High-pressure synthesis at the origin of new developments in silicon clathrate physical chemistry

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## Abstract

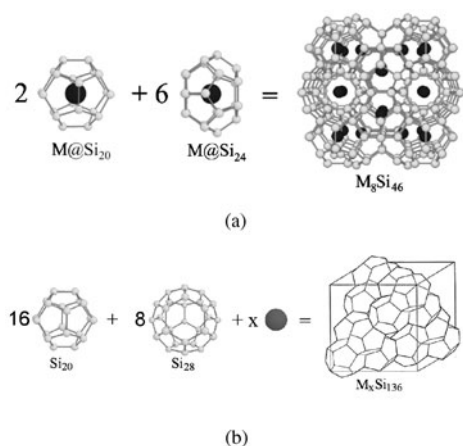
Since their discovery in 1965, various compositions of clathrate phases of silicon have been investigated and have revealed a direct correlation between the doping element and their properties. The recent development of a new synthesis technique using high-pressure and high-temperature (HPHT) conditions allows the synthesis of peculiar clathrate compositions which can show fascinating properties, such as  $\text{Ba}_8\text{Si}_{46}$  which is a  $\text{sp}^3$  silicon-based structure with superconducting characteristics. This work reports the synthesis of the first binary silicon clathrate doped with an electronegative element and prepared using HPHT:  $\text{I}_8\text{Si}_{46-x}\text{I}_x$ . Some chemical and structural results are also presented.

## 1. Introduction

Silicon clathrates structures were obtained for the first time by Cros *et al* in the late 1960s. The synthesis technique used was based on the controlled thermal decomposition of  $\text{MSi Zintl}$  phases (with  $\text{M} = \text{alkali metal}$ ) under vacuum or an inert atmosphere [1]. Two structures were obtained: the type I silicon clathrate  $\text{M}_x\text{Si}_{46}$  ( $x = 8$  for  $\text{M} = \text{Na}, \text{K}$  and  $x = 6$  for  $\text{M} = \text{Rb}$ ) and the type II silicon clathrate  $\text{M}_x\text{Si}_{136}$  ( $\text{M} = \text{Na}, \text{Cs}$  with  $0 < x < 24$ ) were found to be isostructural to gas hydrates such as  $(\text{Cl}_2)_8(\text{H}_2\text{O})_{46}$  and to liquid hydrate such as  $(\text{H}_2\text{S})_{16}(\text{CCl}_4)_8(\text{H}_2\text{O})_{136}$  respectively [2]. These structural analogies extend also to *clathrasils*—a subclass of zeolites—where types I and II silicon clathrates have respectively the same structure as *melanophlogite* and *dodecasil 3C*.

In both structures, the silicon host network is a combination of fullerene-type polyhedra that, stacked together and sharing pentagonal or hexagonal faces, fill up space completely. The basic polyhedron, common to these two structures, is the pentagonal dodecahedron, which is the smallest possible fullerene-type cage.

The silicon host lattice of the  $\text{M}_8\text{Si}_{46}$  structure is composed of two pentagonal dodecahedra  $\text{Si}_{20}$  ( $3m$  symmetry) and six tetrakaidecahedra  $\text{Si}_{24}$  ( $42m$  symmetry), offering eight sites per



**Figure 1.** Construction (a) of the type I silicon clathrate  $M_8Si_{46}$  and (b) of the type II silicon clathrate  $M_xSi_{136}$ .

unit cell for guest atoms that are respectively located at the  $(0, 0, 0)$  and  $(1/4, 1/2, 0)$  positions (figure 1(a)). The corresponding space group is  $Pm\bar{3}n$ . The  $M_xSi_{136}$  structure is based on an arrangement of 16 pentagonal dodecahedra  $Si_{20}$  ( $\bar{3}m$  symmetry) and 8 hexakaidecahedra ( $4\bar{3}m$  symmetry) offering 24 sites per unit cell for the guest atoms, respectively located at the  $(0, 0, 0)$  and  $(3/8, 3/8, 3/8)$  positions (figure 1(b)). The space group is  $Fd\bar{3}m$  [3].

It is only recently that several theoretical and experimental investigations have pointed out some remarkable properties for these materials, notably in the fields of thermoelectric applications [4], magnetism [5] and even wide and pseudo-direct band-gap semiconductors [3, 6, 7]. Moreover, some interesting work showed recently that the bulk moduli for the two types of structure are a few per cent inferior to that of the diamond form of silicon. Therefore silicon clathrates are low-compressibility materials [8]. The multiplication of potential applications made it essential to develop the synthesis of these compounds in order to extend the doping of the silicon network to other elements.

A radically different technique using high-pressure and high-temperature (HPHT) conditions has been recently developed in order to synthesize new silicon clathrates. One of our biggest successes was the synthesis of a silicon clathrate only doped with barium, and showing type II superconducting properties up to  $T_c = 8$  K, which is exceptional, as the host lattice is only formed of  $sp^3$  hybridized silicon [9]. This paper will present another breakthrough in this search for new silicon clathrate materials by reporting the first silicon clathrate doped with an electronegative element:  $I_8Si_{46-x}I_x$ .

## 2. Synthesis

Silicon powder and iodine were mixed in various molar ratios, and finely ground. The mixture was placed in a h-BN cell (8 mm in inner diameter and 6 mm in length) which was in turn placed in a carbon tube heater and in a pyrophyllite cube as a pressure medium. A cubic multi-anvil press was used (Riken model CP10). The BN cell was heated electrically by the carbon heater and the temperature was monitored by a thermocouple placed under the cell. A synthesis using a stoichiometric mixture of  $I/Si = 8/46$  and a pressure of 5 GPa at  $700^\circ\text{C}$  for 1 h gave a mixture of many phases: diamond silicon and clathrate as major phases and air-sensitive iodides  $SiI_2$  and  $SiI_4$  as minor phases. The iodides could be washed away by ethanol. In order to improve the ratio of clathrate formation, we modified the experimental conditions ( $P$ ,  $T$  and  $I/Si$  ratio) and this resulted in drastic changes of the relative ratios of the various phases

**Table 1.** The effect of the insertion of a seed on the clathrate synthesis yield.  $\Delta a$  is the difference in lattice parameters between the seed and  $I_8Si_{46-x}I_x$ . The percentage given for clathrate and silicon are calculated using the Brindley formulae using relative height of XRD peaks. These values are obtained after washing away all other silicides. ( $\epsilon$ ,  $w$ ,  $m$  stand for traces, weak and moderate quantities.)

Seed	$\Delta a$ (Å)	$SiI_x$	% clathrate	% Si
None	—	$m$	42	58
$Ba_8Si_{46}$	0.089	$w$	77	23
$Ba_8Ag_6Si_{40}$	0.031	$\epsilon$	82	18
$Ba_8Ag_{2.5}Si_{43.5}$	0.010	$\epsilon$	89	11
$I_8Si_{46-x}I_x$	0	$\epsilon$	87	13

obtained. At a lower temperature of 500 °C under 5 GPa, the major phases were Si,  $SiI_2$  and  $SiI_4$  with a small portion of clathrate. At a lower pressure of 3 GPa, only  $SiI_2$  and Si were found. The use of higher molar ratios of iodine to silicon ( $I/Si = 1/2$ ) at 5 GPa and 700 °C, gave no clathrate phase; the major phase was  $SiI_4$ . Even in the optimum condition ( $P = 5$  GPa,  $T = 700$  °C,  $I/Si = 8/46$ ), the yield of clathrate never exceeded 42% in weight after washing.

Surprisingly, however, an addition of a very small quantity of silicon clathrate to the starting mixture ( $I/Si = 1/5.75$ ) remarkably increased the yield of the clathrate formation. Defining  $\Delta a$  as the lattice parameter difference between iodine-doped silicon clathrate and the silicon clathrate added to the starting material, table 1 represents the ratio of the various phases obtained after a treatment at 5 GPa, 700 °C for 1 h. These results show undoubtedly that the addition of a seed is greatly effective for the growth of the crystals: the addition of only 1% of iodine-doped silicon clathrate resulted in an increase of the yield of the clathrate formation up to 90%.

The iodine-doped silicon clathrate is stable in acid, like other binary silicon clathrate compounds. It stays unreactive in 1 M HCl although it decomposes in the very aggressive HF/HNO<sub>3</sub> solution. It is also more stable than diamond silicon in hot alkali solution; therefore it was possible to remove most of the remaining silicon using some 0.2 M sodium hydroxide solution. The resulting sample is a very fine powder.

By using a scanning electron microscope, we were not able to observe single crystals larger than 2–3  $\mu m$ , preventing us from performing a single-crystal structural characterization. In order to grow some larger crystals under pressure, more investigations concerning the synthesis were carried out. The starting material was mixed in a ratio 1/1 with  $BiI_3$ . After a 5G Pa, 1000 °C HPHT treatment, the final product was composed of silicon clathrate as a major phase, with  $BiI_3$ , elemental Bi and binary and quaternary silicon iodides as minor phases. It is important to note that all the silicon was consumed. In the previous synthesis, the overconsumption of iodine provoked by the formation of the  $SiI_x$  iodides led to a lack in iodine (some silicon remained). Here, the decomposition of  $BiI_3$  compensates and gradually provides the system with iodine, favouring the clathrate formation. After a washing in alcohol and HCl, well faceted microcrystals of pure iodine doped-silicon clathrate were obtained. However, no usable single crystal large enough for single-crystal investigation was found.

### 3. Characterization

The sample was decomposed by a concentrated HF/HNO<sub>3</sub> solution in a sealed polytetrafluoroethylene (PTFE) container at 70 °C. Once the dissolution of the silicon was complete, the solution was diluted in boric acid to inhibit the activity of HF (silane formation).

A Perkin-Elmer Optima 3000 apparatus was used to perform some inductively coupled plasma spectroscopy (ICP) and to determine the silicon content. To determine the iodine concentration using ICP spectroscopy, a sodium thiosulphate solution was used to dissolve the iodine crystals. The measurements showed an iodine content of  $48.6 \pm 1.4\%$  corresponding to a formula  $I_{9.5 \pm 0.5}Si_{44.5 \pm 0.5}$  for 54 atoms. The validity of this result was verified by a recovery of the total mass of 97%. In order to double check this composition, some of the sample was heated up to 800 °C under high vacuum conditions for several hours. The only deposit observed in the vacuum line was attributed to iodine. The corresponding weight loss was  $48.1 \pm 1.0\%$  of the initial weight. This value is in very good agreement with the previous result obtained by ICP spectroscopy.

In order to perform structural analysis, a powder diffraction pattern was collected every  $0.02^\circ$  over the range  $25\text{--}120^\circ(2\theta)$  in a step scan mode with a time of acquisition of 0.6 s per point. The apparatus used was a MAC Science model M18XHF spectrometer using graphite monochromated Cu  $K\alpha$  radiation. In the measurement range, 342 reflections were obtained on the basis of a cubic cell with  $a = 10.4195(7)\text{\AA}$ , which is to our knowledge the highest value ever observed for a binary silicon clathrate. The space group  $Pm\bar{3}n$  was assumed. In this framework, there are five independent sites: three host lattice sites (6c, 16i and 24k positions) and two guest atom sites (2a and 6d positions in the centres of the cages) [10]. Various structural hypotheses, concerning the sites occupied by the extra  $x$  iodine atoms in  $I_xSi_{46-x}$ , have been investigated. The only reasonable fit ( $S = 2.06$ ,  $R_{wp} = 0.11$ ) was obtained with a structural model in which the iodine occupies all silicon cages (2a and 6d positions) and 11% of the 16i lattice positions. The other hypothesis, where some of the iodine replaces silicon in the 6c and 24k positions, led to very strong disagreement between the calculated and experimental data. Some preliminary investigations concerning the electrical properties of  $I_xSi_{46-x}$  indicated the absence of any superconducting behaviour down to 2 K and showed that this material is insulating.

#### 4. Conclusions

This work shows, by the discovery of a silicon clathrate doped with iodine, that HPHT synthesis opens new fields to explore in silicon clathrate chemistry. The strong relation between the material's characteristics and its doping is a powerful motivator for the development of new compositions: elements of other columns of the periodic table are to be considered as potential guests for these peculiar silicon networks. Many more doped silicon clathrates may be discovered in the near future.

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