High pressure synthesis of an iodine doped silicon clathrate compound

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A silicon clathrate compound doped with an electronegative element, $I_8Si_{46-x}I_x$ (x = 1.5 ± 0.5), has been prepared for the first time using high pressure and high temperature conditions.

In the late 1960s, alkali-metal doped silicon clahrate compounds (M_8Si_{46} and M_xSi_{136}) were prepared by the thermal decomposition of the Zintl phase MSi (M = Na, K, Rb, Cs) under vacuum or inert atmosphere.[1] The two compounds were isostructural with the clathrate hydrates of type I (or gas hydrate) and type II (or liquid hydrate), respectively.[2] The silicon lattice of the M_8Si_{46} structure (type I) is composed of two pentagonal dodecahedra Si_{20} and six tetrakaïdecahedra Si_{24}, offering eight sites per unit cell for guest alkali atoms.[3] Fig. 1 shows the two types of polyhedra connected by a common pentagonal face.

At the period of their discovery, silicon clathrates did not raise any special interest except for their peculiar crystal structures. However, the discovery of carbon clusters, fullerene, and the superconducting properties of the intercalation compounds M_3C_{60} (M = alkali metals) suddenly raised the interest for silicon clathrates: these latter being constructed of an assembly of the smallest possible fullerene type cages.[4] This led to active research of new silicon clathrates and to the discovery of the first superconducting silicon clathrate, $(Na,Ba)_xSi_{46}$ in 1995,[5] which is also the first superconductor composed of an sp^3 Si tetrahedral network. Much attention has also been paid to the thermoelectric properties of some types of clathrate compounds, originating from their special rattling structure.[6]

Very recently, a new synthesis route for silicon clathrates has been developed, *i.e.* high pressure and high temperature (HPHT) synthesis; a silicon clathrate doped with only barium, Ba_8Si_{46}, was obtained for the first time as a bulk phase under a pressure of 3 GPa and at 800 °C.[7] This compound showed a superconductive transition (T_c) at 8.0 K (highest T_c ever found in silicon clathrates). Another type of silicon clathrate, $Ba_{24}Si_{100}$, isostructural with K_6Sn_{25} was also prepared under a pressure of 1.5 GPa at 800 °C.[8] Note that these two new compounds can only be synthesised using high pressure conditions unlike their germanium analogues, Ba_8Ge_{43} and $Ba_{24}Ge_{100}$.[9,10] The iodine doped germanium clathrate $I_8Ge_{46-x}I_x$ with x = 8/3 was synthesised more than ten years ago by thermal decomposition of germanium diiodide by Nesper's group.[11] In this context of the studies of silicon and germanium clathrate compounds, we have focused our research on the synthesis of iodine doped silicon clathrate with the aid of HPHT conditions, the first silicon clathrate structure hosting an electronegative element.

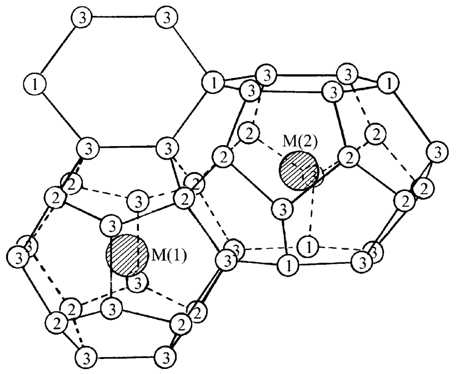

Fig. 1 Schematic illustration of the interconnected polyhedra forming the clathrate type I structure with guest atoms M(1) and M(2). Non-equivalent silicon sites are shown: Si(1), 6c; Si(2), 16i; Si(3), 24k.

Silicon powder (Katayama chemical, 99.999%, 200 mesh) and iodine (Katayama chemical, 99.8%) 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 media. 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 °C for 1 h gave a mixture of many phases: Si 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. The change in the conditions (P, T and I/Si ratio) resulted in a drastic change of the relative ratios of the various phases 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 under the optimum conditions (P = 5 GPa, T = 700 °C, I/Si = 8/46), the yield of clathrate never exceeded 42 wt%. Surprisingly, however, an addition of only 1% of iodine doped silicon clathrate to the starting mixture (I/Si = 1/5.75) remarkably increased the yield of the clathrate formation up to 90% at P = 5 GPa, T = 700 °C, for 1 h. This suggests that the addition of seed is greatly effective for the growth of the crystals.

The new clathrate compound was found to be stable in acidic solutions like other binary clathrate compounds:[1] it was unreactive in 1 M HCl solution, although it decomposed in a concentrated HF–HNO_3 solution. In hot alkali solution (0.2 M NaOH) silicon dissolves readily but the clathrate phase is much less reactive. This finding provided us with a powerful tool to remove most of the remaining silicon from the final product. The resulting iodine doped clathrate was very fine powder, and the suspension in water had a bright orange colour. The powder sample was separated using a PTFE filter.

The clathrate sample was decomposed by a concentrated HF–HNO_3 solution in a sealed PTFE container at 70 °C. The silicon component was dissolved in the solution, and diluted with a saturated boric acid solution for analysis by inductively coupled plasma atomic emission spectroscopy (ICP, Perkin-Elmer Optima 3000). The iodine component was precipitated in the form of elemental crystals, which could be dissolved by adding potassium iodide. The precipitation of iodine crystals suggested that the iodine was included as electrically neutral atoms in the clathrate. To determine the iodine concentration by ICP, a separate solution was prepared and the iodine precipitate was dissolved with a sodium thiosulfate solution. The ICP results gave the following formulation: $I_{9.5 \pm 0.5}Si_{44.5 \pm 0.5}$ (*i.e.* an iodine wt% of 48.6 ± 1.4) with a total recovery of 97%. On heating the clathrate sample up to 800 °C for several hours under high vacuum ($< 10^{-4}$ Torr), a wt% loss of 48.1 ± 1.0 was observed. This value was in good agreement with the chemical analysis data.

X-Ray powder diffraction (XRD) data (Fig. 2) were measured using graphite monochromated Cu-Kα radiation and were collected at every 0.02° over the range $2\theta = 25$–120°. All reflections were indexed on the basis of a cubic unit cell with $a = 10.4195(7)$ Å, which is the largest lattice constant so far observed for binary silicon clathrates. The crystal structure was determined by X-ray Rietveld refinement using Fullprof.[12] The space group ($Pm\bar{3}n$) of type I clathrate was assumed, and the refinements were carried out on the basis of various structural hypotheses. The only reasonable fit was obtained with a structural model, in which iodine atoms occupy all the silicon cages (2a and 6d) and 11% of the Si(2) sites of the network (see Fig. 1). The corresponding stoichiometry ($I_8Si_{44.2}I_{1.8}$) is concordant with the chemical analysis data. The replacement of the Si(1) or Si(3) sites with iodine led to very strong disagreement beween the calculated and the experimental data.

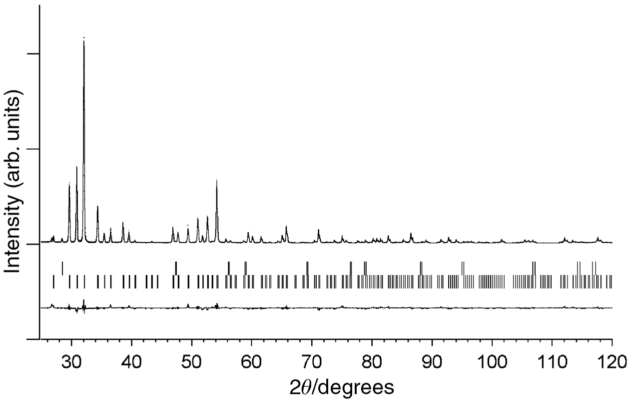

Fig. 2 Plot of the X-ray diffraction data for $I_8Si_{46-x}I_x$ with $x = 1.8$. Discontinuous and continuous lines represent, respectively, the experimental data points and the calculated spectra. The upper tick marks indicate the calculated reflection positions for some traces of silicon and the lower tick marks the calculated reflection positions for the clathrate phase. The lower continuous line represents the difference.

It was reported that in the germanium doped silicon clathrate ($I_8Ge_{43.3}I_{2.7}$), some iodine was present in the Si(1) sites. Therefore it should be noted that although the compositions of the two iodine doped clathrates are similar, replacement of silicon does not occur in the same sites. The coordinates of Si(2) and Si(3) sites were also refined and led to the following positions respectively: 16i (x, x, x) with $x = 0.1831(5)$ and 24k ($0, y, z$) with $y = 0.3099(8)$ and $z = 0.1161(8)$. Although the fit is good enough to be sure about the atomic repartitions and positions ($S = 2.06$, $R_{wp} = 0.11$, see also Fig. 2), an effort is now being carried out to obtain single crystals for a more precise structural study.

Some preliminary results of the physical properties showed that the new clathrate was an electric insulator as estimated from its orange color, and showed the absence of superconductivity down to 2 K.

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Notes and references

1 C. Cros, M. Pouchard and P. Hagenmuller, *C.R. Acad. Sci. Paris*, 1965, **260**, 4764.
2 J. S. Kasper, P. Hagenmuller, M. Pouchard and C. Cros, *Science*, 1965, **3704**, 1713.
3 E. Reny, P. Gravereau, C. Cros and M. Pouchard, *J. Mater. Chem.*, 1998, **8**, 2839.
4 C. Cros, E. Reny and M. Pouchard, *Mol. Cryst. Liq. Cryst.*, 1998, **310**, 199.
5 H. Kawaji, H. Horie, S. Yamanaka and M. Ishikawa, *Phys. Rev. Lett.*, 1995, **74**, 1427.
6 G. S. Nolas, J. L. Cohn, G. A. Slack and S. B. Schujman, *Appl. Phys. Lett.*, 1998, **73**, 178.
7 S. Yamanaka, E. Enishi, H. Fukuoka and M. Yasukawa, *Inorg. Chem.*, 2000, **39**, 56.
8 H. Fukuoka, K. Ueno and S. Yamanaka, *J. Organomet. Chem.*, 2000, **611**, 543
9 H. Fukuoka, K. Iwai and S. Yamanaka, personal communication.
10 H. Fukuoka, K. Iwai, S. Yamanaka, H. Abe, K. Yoza and L. Häming, *J. Solid State Chem.*, 2000, **151**, 117.
11 R. Nesper, J. Curda and H. G. von Schnering, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 350.
12 J. Rodriguez-Carjaval, *Collected Abstracts of Powder Diffraction Meeting, Toulouse (France)*, 1990, p. 127.