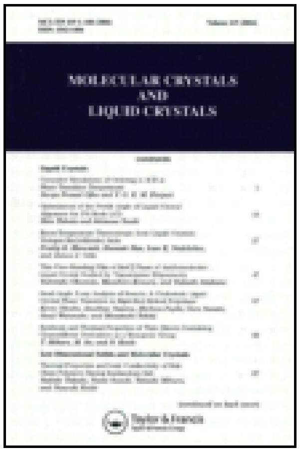

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Recent Developments on the Clathrates M_8Si_{46} and M_xSi_{136} ($M = Na, K, Rb, Cs, Ba$; $0 \le x \le 24$) as Inclusion Compounds of Alkali Metals in Connected Fullerene-like Cages of Silicon

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Recent Developments on the Clathrates M_8Si_{46} and M_xSi_{136} (M = Na, K, Rb, Cs, Ba ; $0 \le x \le 24$) as Inclusion Compounds of Alkali Metals in Connected Fullerene-like Cages of Silicon

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In the structure of the clathrate-type silicides M_8Si_{46} and M_xSi_{136} (M = Na, K, Rb, Cs, Ba ; $0 \le x \le 24$), the silicon atoms form 3D covalent sublattices which correspond to the association of two kinds of fullerene-like cages : Si_{20} and Si_{24}, and Si_{20} and Si_{28} respectively. The M atoms are trapped at the centre of all or part of the two different cages and are distributed according to a A15 and a C15 type sublattice, respectively. Due to their clathrate-type structure, these silicides exhibit original and interesting physical properties. The two structures are described and a short review is given on the previous and recent developments on these cage-like compounds.

Keywords : clathrates, fullerenes, inclusion compounds

INTRODUCTION

The discovery of the fascinating structures and physical properties of the fullerene forms of carbon, as well as their intercalation compounds M_3C_{60} or MM'_2C_{60} (M,M' = alkali metals) gave rise to an increasing interest for cage-like structures of other covalent elements. Clathrate structures of silicon M_8Si_{46} - or $M_2M'_6Si_{46}$ - and M_xSi_{136} (M,M' = Na, K, Rb, Cs, Ba ; $1.5 \le x \le 24$), which have been synthesized in the late sixties, are isostructural of the gas (type I) and liquid (type II) hydrates, respectively [1-4]. These structures can be considered as inclusion compounds of alkali metals - or alkali metals and baryum - in connected fullerene-like cages of silicon : Si_{20}, Si_{24} and Si_{28}. They have striking similarities with the intercalation compounds of alkali metals or alkaline earth metals, such as M_3C_{60} [5], but they exhibit very original structural, chemical and physical properties, due to their clathrate-like character.

The aim of this article is to give a short review on the previous and recent developments on these compounds, with an emphasis on their interest on the fundamental point of view and their potential use as electronic materials.

STRUCTURE OF THE SILICON CLATHRATES

Each structure is characterized by a silicon host lattice which consists of two kinds of face sharing polyhedra- or cages- having 12 pentagonal faces and n hexagonal faces, with n = 0, 2 and 4, a condition which is fulfilled in all the fullerene-type polyhedra. These silicon polyhedra correspond respectively to the pentagonal dodecahedron (fig. 1-a), the tetracaidecahedron (fig. 1-b), and the hexacaidecahedron (fig. 1-c), and the following clusters : Si_{20} (n = 0), Si_{24} (n = 2) and Si_{28} (n = 4). The M atoms are trapped at the center of the cages, hence the name of clathrates.

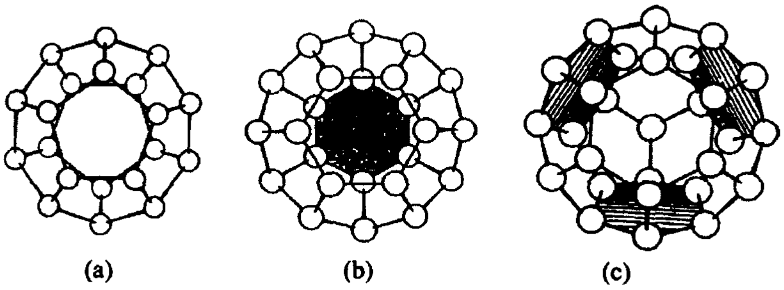

FIGURE 1 The three fullerene-like cages (a) Si_{20}, (b) Si_{24} and (c) Si_{28}

In the structure of M_8Si_{46}, two Si_{20} share faces with six Si_{24}. This arrangement form a large primitive cubic unit cell with a ≈ 10.20 Å, and a total of 46 silicon atoms (fig. 2-a). The M atoms are distributed according to a A15 type-structure, with 2M in the 2a sites (centres of the pentagonal dodecahedra) and 6M in the 6c sites (centres of the tetracaidecahedra). The space group is $Pm\bar{3}n$ and it is noteworthy that this structure is isostructural of Ba_3C_{60} and Cs_3C_{60} [5]. When all the available sites are occupied, the formula is M_8Si_{46} if the M atoms are of the same type, or $M_2M'_6\ Si_{46}$ if they are of two different kinds [6]. The formula is M_6Si_{46} when the largest Si_{24} cages are only occupied.

In the structure of M_xSi_{136} sixteen Si_{20} share faces with eight Si_{28}. This arrangement leads to a large fcc unit cell of ≈14.60 Å and a total number of 136 silicon atoms (fig. 2-b). The M atoms are distributed according to a C15 type-structure, with 8M in 8a sites (centres of the Si_{28} cages) and 16M in the 16d sites (centres of the Si_{20} cages). The space group is $Fd\bar{3}m$. When all the available sites are occupied, the formula is $M_{24}Si_{136}$; it is M_8Si_{136} if the smaller Si_{20} cages are empty.

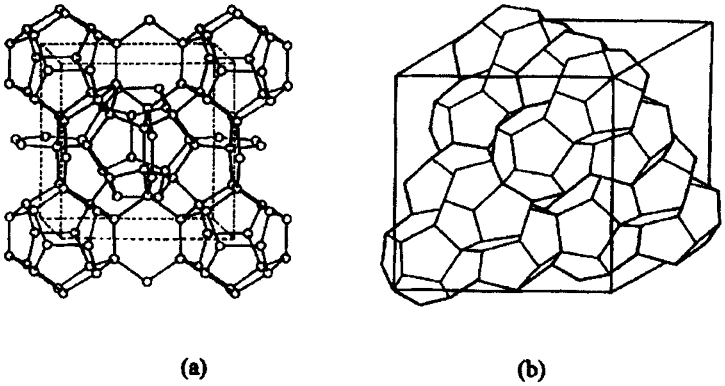

FIGURE 2 Schematic view of the silicon lattice in (a) M_8Si_{46} and (b) M_xSi_{136}

In the covalent 3D network of both structures, silicon atoms are tetrahedrally linked together. The bonding angle is close to 109.47°, and the average Si-Si distance (≈ 2.37 Å) is very slightly longer than in diamond type silicon (2.35 Å). It is noteworthy that all the adjacent tetrahedra are in "cis" position, whereas they are all in "trans" position in the diamond form of silicon and alternatively in "cis" and "trans" positions in the lonsdaleite form. The empty structures Si_{46} and Si_{136} correspond to two open allotropic forms of silicon with ≈ 17 % less compacity.

As in the case of clathrate hydrates the formation of the structure is essentially governed by the size of the guest species. From the comparizon between the "free radius" of the available sites and the apparent size of the guest species, the alkali atoms seem to be more "atomic-like" than ionized.

PREPARATION AND CHEMICAL PROPERTIES

The silicon clathrates are prepared by careful thermal decomposition of the Zintl-type silicides MSi - or the mixed silicides Na_2BaSi_4 and K_2BaSi_4 - under vacuum or inert atmosphere [1,3,4,6].

The silicon clathrates M_8Si_{46} and M_xSi_{136} are remarkably insensitive to moisture, water and acids, except HF. This behaviour points out that the alkali atoms inside the cages are protected from the outer reagents by the silicon network.

PHYSICAL PROPERTIES

The physical properties, namely magnetic susceptibility, Seebeck effect and conductivity have been previously studied [3,7]. It was observed that the conductivity in these compounds is strongly dependant on the rate of occupancy of the available sites by the alkali atoms. In the fully - or almost fully - occupied structure of Na_8Si_{46}, K_7Si_{46} and $Na_{22}Si_{136}$, a metallic behaviour was observed, whereas a gradual evolution from a semi-conducting to a metallic behaviour was found to occur as a function of x in Na_xSi_{136} from $x = 3$ to $x = 22$. This behaviour was interpreted in more details by Mott [8] and Sim [9], who stated a possible insulator to metal transition at $x = 8$.

Following the discovery of superconductivity in the M_3C_{60} compounds, Roy *et al.* [10] measured the conductivity behaviour of Na_8Si_{46} and Na_xSi_{136} at low temperature, but without success for superconductivity down to 2K. Adams *et al.* [11], Demkov *et al.* [12] and Saito and Oshiyama [13] investigated the electronic structures of the empty and metal doped Si_{46} and Si_{136}, and came to the following conclusions :

(i) the energy differences between the two empty clathrate forms and the diamond-type structure of silicon are very small and of the order of 0.07 eV/atom,

(ii) in the empty clathrate-type structures of silicon, due to the presence of a large amount of pentagonal faces, the indirect band gap is enlarged of ≈ 0.7 eV, which leads to a total gap of about 1.9 eV, i.e. of the same order of magnitude as in porous silicon,

(iii) the presence of alkali or alkaline earth atoms in the doped Si_{46} and Si_{136} clathrates has different effects on the band structure, which depend upon the nature and the occupancy rate of the available sites.

In the recently synthesized codoped clathrate, $Na_2Ba_6Si_{46}$, a strong hybridization of the Ba states with the Si_{46} ones results in a very high density of states at the Fermi level, which was considered of primary importance to explain the superconducting behaviour of this compound ($T_c \approx 4K$) [14].

Complementary studies aimed at a better understanding of the degree of ionization of the alkali and alkaline earth species encapsulated in the cages of the Si_{46} and Si_{136} clathrates have been recently carried out by EPR and NMR [9,10,15-18]. In particular, it has been observed that the Knight shift of the resonance peak of ^{23}Na in $(NaBa)_xSi_{46}$ is compatible with that of metallic sodium (1123 ppm). In the case of Na_9Si_{136} and Na_4Si_{136}, however, two resonance peaks are observed with almost two times larger values of the corresponding shifts. Consequently, the guest species seem to be better described as having their 3s electrons localized, as it was previously suggested [7,18].

In conclusion, due to the above reported properties, the empty and doped silicon clathrates appear as highly interesting materials, both on the fundamental point of view and potential use as new electronic materials.

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