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Oxidation of M_4Si_4 (M = Na, K) to Clathrates by HCl or H_2O

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An intriguing question related to the chemistry of Zintl phases is whether their ionic description is truly reflected in their chemical behavior and not merely a nominal structural description. It had been presumed that the oxidation of these compounds in protic acids would simply lead to stable elemental and oxide/hydroxide phases. Our investigations on the redox reactions of typical Zintl phases, the alkali metal monosilicides, with gaseous protic agents such as HCl or H_2O has resulted in the synthesis of clathrate-I silicides, $Na_{8-x}Si_{46}$ and $K_{8-x}Si_{46}$. This is the first report of a high-yield scalable synthesis of clathrate silicides based on a controlled oxidation of the monosilicides, Na_4Si_4 or K_4Si_4. The key step in this process is related to the recently reported synthesis of clathrate-II germanium $\square_{24}Ge_{136}$ in an ionic liquid.[1]

Clathrate-I compounds based on group 14 elements are expected to be promising materials for a variety of applications such as in thermoelectricity and optoelectronics.[2−4] Generally, difficulties in preparing clathrates in high yields are still an important drawback for any expected application. So far, Si clathrates could only be obtained by high-pressure synthesis[5] or thermal decomposition of the alkali metal monosilicides.[6,7] Current thermal decomposition routes of precursor silicides exhibit low yields of the desired product. Furthermore, α-Si is usually formed as a byproduct of the decomposition. A simple direct synthesis of binary clathrates, $M_{8-x}Si_{46}$, from the elements has not yet been reported. The reason may be that these clathrates already decompose in closed Ta ampoules under argon atmosphere at around 600 °C, and at lower reaction temperatures it is difficult to achieve equilibrium within a reasonable time. The preparation route introduced in this contribution is therefore a promising alternative for the synthesis of intermetallic clathrates.

The clathrate-I structure of $M_{8-x}Si_{46}$ consists of an open framework formed by tetrahedral-bonded silicon atoms (Figure 1). In contrast to α-Si, which forms the diamond structure having hexagonal Si_6 rings with chair configuration, the clathrate-I structure features Si_5 and planar Si_6 rings that cause substantial deviations from ideal tetrahedral bond angles. This allows an arrangement with two different types of cages in the Si framework: Si_{20} formed by 12 pentagons and Si_{24} formed by 12 pentagons and 2 hexagons. The "guest" alkali metal atoms are located within the cages of the framework.

A new low-temperature approach for obtaining a clathrate-like germanium framework was recently reported.[1] Na_4Ge_4 or $Na_{12}Ge_{17}$ were reacted in a 1:1 mixture of $AlCl_3$ and *n*-dodecyltrimethylammoniumchloride (DTAC) at 300 °C to $\square_{24}Ge_{136}$. The silicide precursors Na_4Si_4[8] or K_4Si_4[9] transform into clathrates, $M_{8-x}Si_{46}$, under similar conditions. The product also contains α-Si and unknown amorphous phases. Syntheses at higher reaction temperatures using $AlCl_3$/DTAC are difficult because of uncontrollable decomposition of the ionic liquid. The successful synthesis of clathrate-I silicides requires an oxidizing agent that would react in a controlled manner at the appropriate temperatures. High yields of crystalline $M_{8-x}Si_{46}$ were subsequently achieved by the oxidation of M_4Si_4 with gaseous HCl:

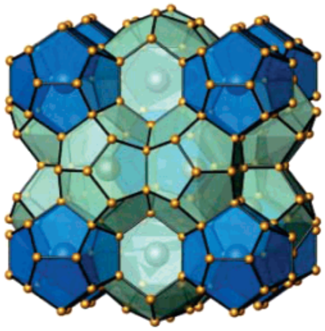

Figure 1. Crystal structure of $M_{8-x}Si_{46}$; Si_{24} polyhedra (green); Si_{20} polyhedra (blue), M atoms (gray, inside the cages), and Si atoms (brown).

$$11.5M_4Si_4 + 38HCl \rightarrow M_8Si_{46} + 38MCl + 19H_2$$

The oxidation reactions were performed via two different experimental setups:[10]

(1) The finely powdered precursors Na_4Si_4 (≈0.13 mmol) or K_4Si_4 (≈0.08 mmol) were sealed under argon with a 20-fold molar excess of NH_4Cl spatially separated from each other into a Duran-glass tube. The tube was heated for 1 h at 400 °C (Na_4Si_4) or 450 °C (K_4Si_4). From 160 °C on, NH_4Cl dissociates completely to HCl and NH_3[11,12] (p_{sat}(HCl, 400 °C) ≈ 2.1 bar,[11] p_{tot} ≈ 6 bar).

(2) Gaseous HCl is produced by reaction of $NaHSO_4$ and NaCl in a glass vessel under argon atmosphere at 180 °C. The gaseous HCl is directed via a glass bridge to the reactor containing the monosilicide. The reactor (equipped with a blow-off valve) is heated, for 20 h, at 400 °C in the case of Na_4Si_4 and 450 °C with K_4Si_4. Both setups allow a wider range of synthesis temperature without the limitations originated from the ionic liquid route as previously reported. It is also possible to use larger amounts of the precursors. However, the dependence of the oxidation process on the HCl pressure and the formation of clathrate-II Na_xSi_{136} as a byproduct have not yet been optimized. Furthermore, the reaction is not limited to HCl as the protic agent. Through the use of setup 2 Na_4Si_4 could be oxidized within 20 h at 300 °C with water vapor (p_{sat}(25 °C) ≈ 0.03 bar) to a mixture of silicides with clathrate-I and clathrate-II crystal structures.

The products from both syntheses 1 and 2 were washed with water to remove the metal salts. The dark gray powders were subsequently dried under vacuum at room temperature.

Scanning electron microscopy investigations (Philips XL30, LaB_6 cathode) showed that in both reactions sharp-edged particles and agglomerates with sizes up to 20 μm were formed (Figure 2; see also Supporting Information S1−2). Energy dispersive X-ray

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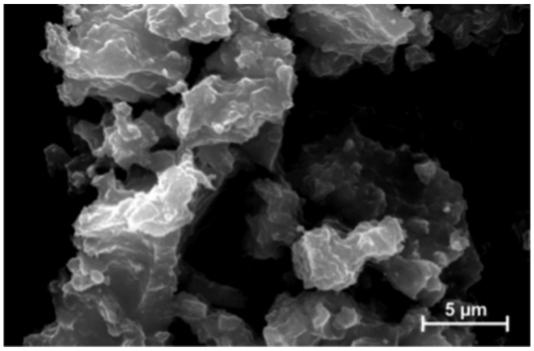

Figure 2. SEM image of $Na_{8-x}Si_{46}$ agglomerates obtained from oxidation of Na_4Si_4 by HCl after 1 h, setup 1. (Au sputtered sample, SE contrast.)

spectroscopy (EDXS; EDAX Si(Li) detector) confirms the presence of solely Na (K) and Si in the products.[13]

After 1 h reaction of Na_4Si_4, through the use of setup 1, the XRPD data revealed a mixture of two crystalline products, clathrate-I $Na_{8-x}Si_{46}$ (≈70 mass %) and clathrate-II $Na_{24-x}Si_{136}$ (≈30 mass %). No α-Si was detected in the products (page S3). Full-profile Rietveld refinement of the clathrate-I crystal structure showed full occupancies at the three Si sites.[14] Both Na positions were found to be partially occupied giving a final composition of $Na_{6.2(1)}Si_{46}$ (page S4). The observed lattice parameter of $a = 10.199(1)$ Å is close to that reported in the literature for Na_8Si_{46} (page S6).[7,15] The crystal structure of the minor byproduct, clathrate-II Na_xSi_{136}, was refined only as a first approximation. Its silicon framework seems to be fully occupied, and of the two possible cation positions only one is occupied (partially) leading to a composition of $Na_{0.6}Si_{136}$,[16] thus revealing a viable route to the formation of the empty silicon clathrate-II. Through the use of setup 2, Na_4Si_4 was reacted for 20 h to form a mixture of clathrate-I $Na_{8-x}Si_{46}$, $a = 10.198(1)$ Å, and clathrate-II Na_xSi_{136}, $a = 14.645(1)$ Å. XRPD indicated that crystalline silicon is not formed.

The 1 h treatment of K_4Si_4, using setup 1, results in only one crystalline product (page S3), clathrate-I $K_{8-x}Si_{46}$ with $a = 10.278(1)$ Å and an amorphous phase. The occupancy of the cation positions in this case is higher compared with the Na compound, and yields a composition of $K_{7.0(1)}Si_{46}$ (page S5).[17] Through the use of setup 2, K_4Si_4 was reacted to form clathrate-I $K_{8-x}Si_{46}$ with $a = 10.280(1)$ Å (page S6).

To distinguish the effects of thermal decomposition from the oxidation with HCl, the stability of the precursors was investigated for all reaction temperatures without an oxidizing agent. After 1 h treatment (Na_4Si_4 at 400 °C; K_4Si_4 at 450 °C), XRPD indicated that both precursors remain unchanged. Only thermal treatments for 20 h result in significant amounts of clathrate-I with residues of M_4Si_4. Moreover, the lattice parameter of $K_{8-x}Si_{46}$ obtained from thermal decomposition of K_4Si_4, $a = 10.267(1)$ Å, is smaller than that of the product obtained from the reaction with HCl ($a = 10.280(1)$ Å). These results prove that the $M_{8-x}Si_{46}$ phases obtained with both experimental setups result from the reaction of M_4Si_4 with HCl.

Differential scanning calorimetry measurements in welded Nb ampoules exhibit an exothermic effect at 594 °C for $Na_{8-x}Si_{46}$ and at 716 °C for $K_{8-x}Si_{46}$ (obtained from setup 1), indicating the metastable character of both clathrates. Annealing $Na_{8-x}Si_{46}$ at 600 °C for 18 h results in a partial decomposition of the clathrate-I compound to α-Si (XRPD data). $K_{8-x}Si_{46}$ is completely decomposed to α-Si within 18 h at 720 °C.

Magnetic susceptibility measurements[18] $\chi(T) = M/H$ on $Na_{8-x}Si_{46}$ and $K_{8-x}Si_{46}$ samples consistently showed a diamagnetic substance with traces of a ferromagnetic impurity. After taking the impurities into account, the molar susceptibilities were calculated to be $\chi(300\ \mathrm{K}) = -5 \times 10^{-4}$ emu mol^{-1} for $Na_{8-x}Si_{46}$ and $\chi(300\ \mathrm{K}) = -3 \times 10^{-4}$ emu mol^{-1} for $K_{8-x}Si_{46}$. The electrical resistivity $\rho(T)$ of a cold pressed sample of $K_{8-x}Si_{46}$ powder is almost temperature-independent with $\rho \approx 0.025\ \Omega$ m.[19] No phase transition or superconductivity is observed above 1.8 K. For the composition $M_{8-x}Si_{46}$, a bad-metallic behavior and a Pauli-paramagnetic contribution to $\chi(T)$ is expected. The observed diamagnetic behavior of the filled clathrates can be attributed to large additional diamagnetic contributions from ring currents.[20]

We have demonstrated a viable controlled oxidation of Zintl phases that results in metastable compounds with open-framework structures. The synthesis route to silicon clathrates is a general route and can therefore be applied to Zintl-phases of other elements, as well as, other saltlike intermetallics.

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Supporting Information Available: SEM images, XRPD patterns and crystallographic data of $Na_{6.2(1)}Si_{46}$ and $K_{7.0(1)}Si_{46}$, comparison and evaluation of lattice parameters with literature data. The material is available at http://pubs.acs.org.

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(13) A low intensity Cl *K* line, the only significant minority line beside small contribution of O or N *K* line, indicates small residues of NH_4Cl or MCl.

(14) Crystallographic data of $Na_{6.2(1)}Si_{46}$: space group Pm-3n, $a = 10.199(1)$ Å; 1.70(4) Na in 2a 000; 4.50(5) Na in 6c 1/4 1/2 0; 6 Si in 6d 1/4 0 1/2, 16 Si in 16i xxx, $x = 0.1840(3)$, 24 Si in 24k 0yz, $y = 0.3053(3)$, $z = 0.1184(4)$.

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(16) Crystallographic data of $Na_{0.6}Si_{136}$: space group $Fd\bar{3}m$, $a = 14.645(1)$ Å; 0.6(3) Na in 8b 3/8 3/8 3/8; 8 Si in 8a 7/8 7/8 7/8; 32 Si in 32e xxx, $x = 0.7832(6)$, 96 Si in 96h xxz, $x = 0.8200(4)$, $z = 0.6324(5)$.

(17) Crystallographic data of $K_{7.0(1)}Si_{46}$: space group $Pm\bar{3}n$, $a = 10.278(1)$ Å; 1.60(2) K in 2a 000; 5.40(4) K in 6c 1/4 1/2 0; 6 Si in 6d 1/4 0 1/2, 16 Si in 16i xxx, $x = 0.1842(3)$, 24 Si in 24k 0yz, $y = 0.3061(4)$, $z = 0.1180(4)$.

(18) Magnetization was measured at various external fields between 100 Oe and 70 kOe (1.8−400 K) in a SQUID magnetometer (MPMS XL-7, Quantum Design) on polycrystalline samples ($m \approx 4.5$ mg). The contribution of the glass sample holder was subtracted.

(19) The electrical resistivity measurements were performed on a cuboid-shaped cold-pressed sample, annealed at 300 °C. Conventional dc four-point method, 4−320 K; inaccuracy of absolute values are ±20 %.

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