Synthesis and Characterization of Stable Stoichiometric Clathrates of Silicon and Germanium: $Cs_8Na_{16}Si_{136}$ and $Cs_8Na_{16}Ge_{136}$

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The search for new and better thermoelectric materials has recently brought to light a somewhat forgotten class of compounds, the clathrates of group 14.[1] This and some purely theoretical interest in these and similar structural types have instigated much research on their electronic, magnetic, spectral, and conducting properties.[2,3] Furthermore, renewed interest in these systems was sparked by the recent discovery of superconductivity in a Na−Ba−Si compound with the clathrate-I structure.[4] Last, the clathrates are a step closer to porous silicon and the valuable optical properties that come with it.[5] All of this interest has led to the search for reliable and reproducible ways for the synthesis of such silicon and germanium clathrates in high yields and with defined stoichiometry. We have taken a rational approach to this synthetic problem realizing that the two types of cavities in the structure of clathrate-II, $A_8B_{16}E_{136}$ (A and B = cavities, E = element of group 14), are of quite different dimensions, and therefore stabilization of the structure would require very different cations. Clearly, cations of similar sizes will facilitate formation of the other clathrate structure, that of clathrate-I ($A_2B_6E_{46}$), where the cavities are very similar. Thus, the clathrate-I structure is predominant in the binary systems with alkali metals where cations of only one size are available. Such binaries are reported in the systems (Na or K)−Si, K−Ge, and (K, Rb, or Cs)−Sn where the alkali metal is found in both cavities.[1a,6] This and the similar stoichiometries of the two clathrates explain why reactions designed to produce clathrate-II in the binary systems usually yield clathrate-I. Such synthetic difficulties have led to the development of a somewhat unconventional approach for making some amounts of clathrate-II. The method uses "controlled" decomposition of the Zintl phases ME (M = alkali metal) at high temperatures and vacuum.[2−5] The process yields inhomogeneous powders with undefined stoichiometry (usually characterized by bulk elemental analysis) and of low quality. The product is usually a mixture of the two clathrates, unreacted ME, and even the elements, and further purification is necessary in order to separate the phases.[3] Furthermore, small changes in the experimental conditions may result in quite different overall compositions of the mixtures,[3c] and therefore it is very difficult to obtain good control and reproducibility.[4c] Powder diffraction in this case is not a very useful tool for stoichiometry confirmation since the composition could vary substantially from particle to particle without noticeable changes in the lattice parameters due to the rigidity and covalency of the framework. Here we report reproducible synthesis of stoichiometric and completely filled silicon and germanium compounds, $Cs_8Na_{16}Si_{136}$ and $Cs_8Na_{16}Ge_{136}$ (Si_{136} and Ge_{136} hereafter), with the clathrate-II structure type.

The silicon compound was initially identified from a reaction designed to produce $CsNa_2B_3Si_{14}$ but in excess of Cs (intended as a solvent). The three boron atoms were initially included to charge balance for the three alkali-metal cations since a tetrahedrally bonded boron atom has a formal charge of −1. The first few reactions were heated at 950 °C, i.e., well above the boiling point of the cesium solvent (Cs boils at 690 °C). All reactions were carried out in welded niobium containers sealed in evacuated quartz jackets.[7] Later it was determined that there was no boron in the final product and that the synthesis could be carried out at lower temperatures. Thus, high yields of the two compounds can be made from stoichiometric mixtures heated at 550 °C for 30 days (cooled with a rate of 10 °C/h). The products consist of large single crystals of overall polyhedral shape, some of up to ca. 2 mm. Both Si_{136} and Ge_{136} appear bluish and with metallic luster.

The compounds were structurally characterized by single-crystal X-ray diffraction. Data sets were collected with Mo Kα for up to $2\theta_{max}$ = 90 and 100° for Si_{136} and Ge_{136}, respectively, instead of the conventional limit of 50°. This was done in order to refine as precisely and unequivocally as possible all details of the structure such as distances, eventual partial occupancies, mixed sites, etc.[8] It was found that all positions, framework and cationic, in both compounds are fully occupied with no mixing of cations.[9] The Si−Si and Ge−Ge distances range from 2.3584(4) to 2.3924-(5) Å and from 2.4859(7) to 2.5033(9) Å, respectively, and are longer than those in the elements, 2.352 Å for Si and 2.445 Å for Ge. The reason for this does not seem to be the size of the cations since they are somewhat smaller than the cavities. The elongation is more likely due to the available extra electrons, 24 per 136 silicon atoms. They fill partially the silicon conduction band which, of course, is composed of predominantly Si−Si antibonding states. This is supported by the fact that the distances are also longer than those derived theoretically by minimization of the total energy of the empty structure.[2g,4f]

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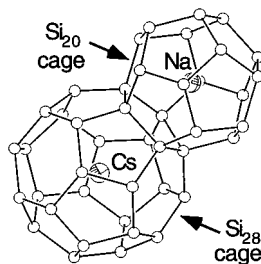
(7) *Caution:* Such reactions lead to high pressure in the niobium ampules and may result in a leak of cesium into the quartz ampule. The latter should be made sufficiently long, and one of its ends should be left protruding outside the furnace for condensation should a cesium leak occur.

(8) Quadrants of X-ray diffraction data from single crystals of Si_{136} (0.2 × 0.2 × 0.2 mm, $2\theta_{max}$ = 90°) and Ge_{136} (0.2 × 0.12 × 0.1 mm, $2\theta_{max}$ = 100°) were collected on CAD4 at room temperature with monochromated Mo Kα radiation. Both compounds diffracted very strongly. (Crystal data: **$Cs_8Na_{16}Si_{136}$,** $Fd3m$, Z = 1, a = 14.7560(4) Å, μ = 36.06 cm^{-1}, d_{calc} = 2.714 g·cm^{-3}, R1/wR2 = 2.01/4.53% for 622 observed ($I \geq 2\sigma I$) and 680 total number of reflections, respectively, and 15 variables; **$Cs_8Na_{16}Ge_{136}$**, $Fd3m$, Z = 1, a = 15.4805(6) Å, μ = 290.41 cm^{-1}, d_{calc} = 5.059 g·cm^{-3}, R1/wR2 = 4.31/8.30% and 9.24/9.81% for 606 observed ($I \geq 2\sigma I$) and 977 total number of reflections, respectively, and 15 variables.) Lattice parameters were also refined from the Guinier powder patterns with Si as an internal standard: 14.758(1) and 15.480(1) Å for Si_{136} and Ge_{136}, respectively.

(9) The deviations from full occupancy for the cationic positions (with the framework positions kept fully occupied) were less than 1σ for both cesium and sodium in both compounds. The occupancies of the framework positions also deviated negligibly from full (with the cationic sites kept fully occupied), with maximums of 1σ for silicon and 2.5σ for germanium.

Figure 1. An ORTEP drawing of $Cs_8Na_{16}Si_{136}$ with the clathrate-II structure (the thermal ellipsoids are drawn at the 98% probability level). The entire framework is built of these fused 28- and 20-atom cages that are centered by Cs and Na, respectively.

As mentioned above, the two types of cavities in this structure are quite different in size (Figure 1). The shortest Cs–Si and Na–Si distances in Si_{136} are 3.9452(2) and 3.1948(1) Å, respectively. The corresponding numbers for Ge_{136} are 4.1356-(5) and 3.3516(1) Å. After subtracting from these distances the van der Waals radii of Si and Ge these numbers become 1.8452-(2) and 1.0948(1) Å for Si_{136}, and 2.0006(5) and 1.2166(1) Å for Ge_{136}. We can compare them with the ionic radii of the alkali metals: 0.95, 1.33, 1.48, and 1.69 Å for Na, K, Rb, and Cs, respectively.[10] Clearly, Rb is too small for the large cavities, and K is too big for the small ones, but apparently Cs and Na fit well for both Si and Ge systems. Our attempts to synthesize Rb_8Na_{16}-(Si or Ge)$_{136}$ and Cs_8K_{16}(Si or Ge)$_{136}$ were unsuccessful. The cavities in clathrate-I are with much closer sizes: 1.34 Å for the larger and 1.18 Å for the smaller holes in the silicon compounds (averaged), 1.45 and 1.26 Å for the germanium analogue, and 1.87 and 1.65 Å for the tin compounds (averaged). Thus, sodium could fit relatively well in both cavities of the silicon compound but would be too small for germanium and tin. Similarly, cesium would fit in either cavity of the tin compound but will be too big for silicon and germanium. None of the single cations, on the other hand, could fit efficiently enough in both cavities of any of the clathrate-II compounds.

Both the silicon and germanium clathrates are remarkably air- and moisture-stable. Furthermore, our extensive studies of the stability of Si_{136} show that it is also stable at extreme conditions. Different tests were performed, and after each test single-crystal data were collected, and the structure and the occupancies of the different sites were refined. In these tests crystals of the compound were (a) washed with water and ethanol; (b) soaked in a mixture of concentrated HCl and H_2SO_4, (c) treated hydrothermally in a 5% HCl in an autoclave at 180 °C for 1 day, (d) heated under vacuum at 900 °C for 1 h in a TGA, and (e) heated in air at 950 °C for a few minutes in a TGA. No weight loss was observed in either of the latter two experiments. The refined structures from the tests showed essentially the same results as those of the as prepared compound, i.e., both the cationic and framework sites were fully occupied.[11] In addition to these, a powdered sample heated at 800 °C under much higher vacuum, ca. 10^{-5} mmHg (below discharge), for 2 days showed no noticeable change both in the lattice parameters and in the relative intensities of the X-ray powder diffraction pattern taken with a Guinier camera. When heated above 800 °C at this vacuum, on the other hand, the product becomes dull gray although the "crystallites" preserve their initial shape. The corresponding diffraction pattern shows

only very diffuse lines of elemental silicon. It should be pointed out that the heatings in air at 950 °C and at 900 °C in low vacuum led to the formation of a seal of glassy material, presumably silicon oxide, on the top of the sample. This seal might have prevented the damage of the material underneath.

The electrons from the alkali metals in these compounds are "extra" since all silicon (germanium) atoms are four-bonded in this structure (just as in diamond). The extra electrons could be either delocalized over the four-bonded network or localized on the alkali metals. The latter are well separated in this structure (Figure 1), 5.217 and 6.118 Å for the closest Na–Na and Cs–Na contacts in Si_{136}, respectively, and no communication between them should be expected. Magnetic and four-probe conductivity measurements indicate metallic behavior which is consistent with complete delocalization of the extra electrons. Both Si_{136} and Ge_{136} showed temperature-independent Pauli-like magnetic susceptibility.[12] The resistivity of cold-pressed pellets of Si_{136} showed typical metal-like behavior, increasing linearly with the temperature.[12] Nevertheless, the samples are relatively poorly conducting, about 50 mΩ·cm at room temperature, consistent with results for silicon clathrate-I.[1b]

Clathrate-like structures of the elements of group 14 were observed and recognized from their X-ray powder diffraction patterns more than 30 years ago. The first single-crystal refinements of the structure of clathrate-I appeared in 1969 and were done on data collected on a Weissenberg camera for the potassium compounds with Si, Ge, and Sn.[6a] The accuracy of the structure has been questioned ever since.[13] It is still not clear whether the compounds are K_8E_{46} or $K_8E_{44}\square_2$ ($\square$ = vacancy) or $K_{8-x}E_{46}$, or anything between, since no better structure determination has been published.[13d,e] More recent single-crystal work on clathrate-I compounds in the Rb–Sn and mixed (K,Cs)–Sn systems has shown that, indeed, some of the framework sites are partially occupied.[6c] Our report on the refined structure of clathrate-II adds some more information on the structural chemistry of silicon and germanium at negative oxidation states. Thus, in the systems alkali-metal(s)–silicon and alkali-metal(s)–germanium, proven to exist by single-crystal X-ray diffraction are E_4^{4-}-tetrahedra, E_9^{4-}-deltahedra (monocapped square antiprisms or tricapped trigonal prisms), and clathrate-I and clathrate-II frameworks (formally E_{17}^{3-} in the latter).[6a,14] Currently under way are more detailed measurements of physical properties of the compounds.

Supporting Information Available: An X-ray crystallographic file for the seven structure refinements, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The magnetizations of four different samples of Si_{136} and one sample of Ge_{136} were measured at a field of 3T over the range 6–295 K on a Quantum Design MPMS SQUID magnetometer. All showed temperature independent paramagnetism. The raw data were corrected for the holder (gelatin capsule and cotton) and for the ion-core diamagnetism of Cs^+, Na^+, Si^{4+}, and Ge^{4+}. The resulting molar magnetic susceptibilities are between 2 and 7×10^{-4} emu/mol for Si_{136} and 6.5×10^{-5} emu/mol for Ge_{136}. Samples measured at low field (50–100 G) did not show superconductivity down to 2 K. Four-probe conductivity measurements were taken on two cold-pressed pellets of Si_{136} down to 10 K. The room-temperature resistivities of the two samples were measured at ca. 48 and 52 mΩ·cm, respectively, while the corresponding numbers at 50 K were 30 and 45 mΩ·cm. The temperature dependence in both cases is very close to linear with slopes (temperature coefficients) of 0.072 and 0.028 mΩ·cm/°C, respectively.

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