Synthesis and Characterization of Type II Silicon and Germanium Clathrates

by

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In memory of Randy.

My first lab mate, and a friend who will be missed.
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# Table of Contents

List of Tables iii  
List of Figures iv  
Abstract vii  

1 Introduction 1  

2 An Overview of Type II Clathrates 6  
  2.1 Structural Features 6  
  2.2 Previous Work 9  
    2.2.1 Electrical Properties 11  
    2.2.2 Thermal and Vibrational Properties 15  
  2.3 Applications 20  

3 Synthesis and Sample Preparation 26  
  3.1 Degassing of Silicides and Germanides 26  
    3.1.1 Preparation of Na$_x$Si$_{136}$ Clathrates 26  
    3.1.2 Preparation of Na$_x$Ge$_{136}$ Clathrates and the New Phase Na$_{1-x}$Ge$_3$ 31  
    3.1.3 Other Silicides and Germanides 32  
  3.2 Direct Synthesis of Cs$_8$Na$_{16}$M$_y$Ge$_{136-y}$ Clathrates (M = Ag, Cu) 34  
  3.3 Partially Filled Type II Ge Clathrates 37  

4 Structural and Chemical Characterization 39  
  4.1 Characterization of Na$_x$Si$_{136}$ Clathrates 39  
  4.2 Characterization of Cs$_8$Na$_{16}$M$_y$Ge$_{136-y}$ Clathrates (M = Ag, Cu) 45  
  4.3 The New Compound Na$_{1-x}$Ge$_3$ 49  

5 Transport Properties 53  
  5.1 Experimental Details 53  
  5.2 Transport Properties of Na$_x$Si$_{136}$ Clathrates 54  
  5.3 Transport Properties of Cs$_8$Na$_{16}$Cu$_y$Ge$_{136-y}$ Clathrates 60  

6 Summary and Future Directions 67
List of Tables

Table 2.1  Comparison of ionic radii of the alkali metals with the approximate van der Waals radii of the empty space in the small (20-atom) and large (28-atom) cages in silicon and germanium type II clathrates, after Bobev and Sevov. 9

Table 2.2  Rattler frequencies in cm$^{-1}$ as determined from Raman scattering, ADPs from single crystal XRD, and theoretical calculations. 18

Table 3.1  Structures of various silicides and germanides and the products obtained by their thermal decomposition. 33

Table 4.1  Structure and composition of Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$. 42

Table 4.2  Preliminary structural data for the novel phase Na$_{0.7}$Ge$_3$, space group P6/m, $a = 15.05399(5)$ Å, $c = 3.96845(2)$ Å. 50
List of Figures

Figure 1.1  An example of the cage-like structure of clathrate materials. 3

Figure 2.1  Structure of the type II clathrate. 7

Figure 2.2  Temperature dependence of resistivity (round symbols) and Seebeck coefficient (square symbols) for polycrystalline samples of Cs$_8$Na$_{16}$Si$_{136}$ (filled symbols) and Cs$_8$Na$_{16}$Ge$_{136}$ (open symbols). 13

Figure 2.3  Arrhenius plot of the resistance for Si$_{136}$. 14

Figure 2.4  Temperature dependent ADPs for (a) Rb$_8$Na$_{16}$Si$_{136}$, (b) Cs$_8$Na$_{16}$Si$_{136}$, (c) Rb$_8$Na$_{16}$Ge$_{136}$, and (d) Cs$_8$Na$_{16}$Ge$_{136}$, determined from single crystal X-ray diffraction. 16

Figure 2.5  Raman scattering spectra of Si$_{136}$ and Cs$_8$Na$_{16}$Si$_{136}$. 17

Figure 2.6  Thermal conductivity of the crystalline silicon clathrate Si$_{136}$ and Cs$_8$Na$_{16}$Si$_{136}$. 19

Figure 2.7  Schematic of a thermoelectric couple for power generation. 22

Figure 2.8  Band diagram schematic of carrier generation in a p-n homojunction. 24

Figure 3.1  Crystal structure of the Zintl phase NaSi, emphasizing the Si$_4^{4-}$ cluster units (blue) and Na$^+$ ions (orange). 27

Figure 3.2  Schematic of the vacuum furnace apparatus designed for degassing of the silicides and germanides, and for further degassing of the clathrates. 28

Figure 3.3  Qualitative representation of phase percentages from products obtained from thermal decomposition of NaGe. 31
Figure 3.4  Temperature schedule for the synthesis of the framework substituted type II germanium clathrates.  

Figure 3.5  Small as-grown crystallites of Cs$_8$Na$_{16}$Cu$_y$Ge$_{136-y}$.  

Figure 3.6  Lattice parameter of Na$_x$Rb$_8$Ge$_{136}$, as measured after vacuum degassing at the indicated temperature.  

Figure 4.1  Simulated theoretical X-ray diffraction patterns for Na$_x$Si$_{136}$ clathrates as a function of the Na content $x$, calculated using the PowderCell computer software.  

Figure 4.2  Refinement of powder XRD data for Na$_1$Si$_{136}$. Peaks associated with Na$_8$Si$_{46}$ and diamond-structure silicon are indicated by arrows.  

Figure 4.3  GSAS fit of the powder XRD data for Na$_8$Si$_{136}$.  

Figure 4.4  Stokes Raman scattering spectra for Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$.  

Figure 4.5  Heat flow as a function of temperature for Na$_x$Si$_{136}$ samples with $x = 0, 1, \text{ and } 8$, determined by DSC measurements.  

Figure 4.6  Powder XRD patterns for Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$ clathrates.  

Figure 4.7  Powder XRD patterns for Cs$_8$Na$_{16}$Cu$_y$Ge$_{136-y}$ clathrates.  

Figure 4.8  Lattice parameter as a function of transition metal content for the Cs$_8$Na$_{16}$Cu$_y$Ge$_{136-y}$ (closed circles) and Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$ (open triangles) clathrates.  

Figure 4.9  A schematic of the structure of NaGe$_3$, viewed along the $c$-axis at a slight tilt.  

Figure 4.10  Powder X-ray diffraction of Na$_1$-$x$Ge$_3$.  

Figure 5.1  Temperature dependent electrical resistivity of Na$_1$Si$_{136}$ (closed circles) and Na$_8$Si$_{136}$ (open circles), along with Cs$_8$Na$_{16}$Si$_{136}$ (closed squares).  

Figure 5.2  Temperature dependent thermal conductivity of Na$_1$Si$_{136}$ (closed circles) and Na$_8$Si$_{136}$ (open circles), along with that of single crystal diamond structure silicon (dashed line).
**Figure 5.3** Low temperature lattice thermal conductivity for single crystalline Sr$_8$Ga$_{16}$Ge$_{30}$ (circles) and Eu$_8$Ga$_{16}$Ge$_{30}$ (squares). 58

**Figure 5.4** Temperature dependence of the electrical resistivity of Cs$_8$Na$_{16}$Cu$_y$Ge$_{136-y}$, with $y = 0$, 5, and 8, indicating the metallic behavior of these materials. 59

**Figure 5.5** Temperature dependence of the Seebeck coefficient of Cs$_8$Na$_{16}$Cu$_y$Ge$_{136-y}$, with $y = 0$, 5, and 8. 61

**Figure 5.6** Temperature dependence of the thermal conductivity for Cs$_8$Na$_{16}$Cu$_y$Ge$_{136-y}$, with $y = 0$, 5, and 8. 62

**Figure 5.7** Verification of losses due to radiation during the thermal conductivity measurement. 64
Synthesis and Characterization of Type II Silicon and Germanium Clathrates

Matthew K. Beekman

ABSTRACT

Clathrate materials comprise compounds in which guest atoms or molecules can be encapsulated inside atomic cages formed by host framework polyhedra. The unique relationship that exists between the guest species and its host results in a wide range of physical phenomena, and offers the ability to study the physics of structure-property relationships in crystalline solids. Clathrates are actively being investigated in fields such as thermoelectrics, superconductivity, optoelectronics, and photovoltaics among others. The structural subset known as type II clathrates have been studied far less than other clathrates, and this forms the impetus for the present work. In particular, the known “composition space” of type II clathrates is small, thus the need for a better understanding of possible compositions is evident. A basic research investigation into the synthesis and characterization of silicon and germanium type II clathrates was performed using a range of synthetic, crystallographic, chemical, calorimetric, and transport measurement techniques. A series of framework substituted type II germanium clathrates has been synthesized for the first time, and transport measurements indicate that these compounds show metallic behavior. In the course of the investigation into type II germanium clathrates, a new zeolite-like framework compound with its corresponding novel crystal structure has been discovered and characterized. This compound can be described by the composition Na$_{1-x}$Ge$_3$ (0 < x < 1), and corresponds to a new binary phase
in the Na-Ge system. One of the most interesting aspects of type II clathrates is the ability
to create compounds in which the framework cages are partially occupied, as this offers
the unique opportunity to study the material properties as a function of guest content. A
series of type II sodium-silicon clathrates Na\textsubscript{x}Si\textsubscript{136} (0 < x < 24) has been synthesized in
higher purity than previously reported for as-synthesized products. The transport
properties of the Na\textsubscript{x}Si\textsubscript{136} clathrates exhibit a clear dependence on the guest content x. In
particular, we present for the first time thermal conductivity measurements on Na\textsubscript{x}Si\textsubscript{136}
clathrates, and observe evidence that the guest atoms in type II clathrates affect the
thermal transport in these materials. Some of the crystalline Na\textsubscript{x}Si\textsubscript{136} compounds studied
exhibit very low thermal conductivities, comparable in magnitude to amorphous
materials. In addition, for the first time clear evidence from transport measurements was
found that resonance phonon scattering may be present in type II clathrates, as is also the
case in the type I subset.
Introduction

The term clathrate refers to any group of materials that has the ability to contain atomic or molecular “guest” species within a “host” network or lattice. The structure of these “inclusion compounds” is such that there exist voids that may be filled by the guest species. Strictly speaking, true clathrates are those compounds which crystallize even in the absence of the guest. Examples include the skutterudites and various oxide zeolites, though many more examples exist in which the host lattice only forms in the presence of the guests. These are sometimes referred to as the crypto-clathrates.\textsuperscript{1} However, the structures discussed in this work are collectively referred to simply as clathrates in the literature.

For more than one hundred years, H\textsubscript{2}O has been known to form the compounds referred to today as the clathrate hydrates, where the host lattice is formed by tetrahedrally coordinated, hydrogen bonded H\textsubscript{2}O molecules in much the same manner as common ice.\textsuperscript{2} Also known as gas or liquid hydrates, these compounds constitute structural phases of ice, and can encapsulate molecules or atoms in voids formed by the crystal structure, such as methane or xenon with compositions (CH\textsubscript{4})\textsubscript{8}(H\textsubscript{2}O)\textsubscript{46} and Xe\textsubscript{8}(H\textsubscript{2}O)\textsubscript{46}, respectively. The methane-containing ice clathrates are naturally occurring and can be found under the sea in Polar Regions, as well as the Gulf of Mexico and the
Caspian Sea. There has been much interest in the potential of these clathrates as a useable source of energy, and it has been suggested that if the huge amounts of methane trapped in this form could be harvested it could potentially replace the world’s entire fossil fuel reserves combined. \(^3\,^4\) Ironically, contributions to global warming have also been speculated due to release of methane from the gas hydrates found in the oceans, \(^3\) and gas hydrates have been known to cause flow assurance and safety problems by forming in oil and gas pipelines. \(^4\) Recently, the potential for ice clathrates as a hydrogen storage medium has also been discussed. \(^5\)

To date, geometrically there are nine main possible structures that fall in the general class of clathrate materials, though experimental examples have not been produced for all of these structures. \(^6\) In addition to the nine basic types, structural variants or derivatives have been reported including isomers or superstructure variants of the type I clathrates. \(^7\,-\,^9\) The crystal structure of the type I clathrate, the structure type that has received the most attention, is shown in Figure 1.1. A structural theme common to all clathrate materials are constituent polyhedra that form the crystal structure. Typically these polyhedra share faces in an arrangement allowing for the inclusion of the guest species inside, and include pentagonal dodecahedra, tetrakaidecahedra, and hexakaidecahedra. For the majority of clathrate materials, the framework consists wholly or partially of the group IV elements silicon, germanium, or tin, with the guest species being alkali or alkaline earth atoms, and the rare earth europium.

It was not until the 1960’s that “inorganic” clathrates were first synthesized and investigated. In a systematic study of the thermal degradation of alkali silicides (e.g.,
Figure 1.1 An example of the cage-like structure of clathrate materials. (a) Crystal structure of the type I clathrate, viewed along the [001] direction at a slight tilt. The simple cubic unit cell is outlined in the upper left. (b) The face-sharing polyhedra that constitute the type I clathrate crystal structure.

NaSi, KSi, etc.), Kasper et al.\textsuperscript{10} reported that cubic phases isostructural with the gas hydrates were formed that were deficient in the alkali metal. These compounds comprised the silicon and germanium analogues to the type I and type II clathrate hydrates. A more thorough report of this work was later given by Cros et al.\textsuperscript{11}

Initially, these silicon and germanium clathrates were interesting due to their unique crystal structure, but the physical properties of these materials were not extensively studied. However, in the past ten years new approaches to materials research have renewed interest in these and similar materials, and clathrates have proved a extremely rich source of varied and often novel phenomena. For example, superconducting,\textsuperscript{12,13,14} thermoelectric,\textsuperscript{1,15} photovoltaic and optoelectronic,\textsuperscript{16,17,18}
magnetic$^{19,20}$ and mechanical$^{21,22}$ properties of clathrates are currently being investigated by several groups. Clathrates such as the type I Na$_2$Ba$_6$Si$_{46}$,$^{12}$ Ba$_8$Si$_{46}$,$^{13}$ and the type IX Ba$_{24}$Ge$_{100}$,$^{14}$ comprise unique superconductors. Type I clathrates such as Sr$_8$Ga$_{16}$Ge$_{30}$ and Eu$_8$Ga$_{16}$Ge$_{30}$ exhibit very low thermal conductivities with glasslike temperature dependences.$^{23}$ Paired with the good electrical properties found in Sr$_8$Ga$_{16}$Ge$_{30}$, clathrates are raising continued interest for thermoelectric applications.$^{15}$ Carbon clathrates, as yet not produced experimentally, have been predicted to be the second hardest materials known to humankind.$^{21}$ Some applications of interest for type II clathrates are discussed in Chapter 2.

In addition to potential applications, clathrate materials continue to be of interest for reasons of basic science as well. From a chemical and physical point of view, these materials allow for the study of the physics of compounds possessing isomorphic structures with greatly varying properties, ranging from metals$^{24,25}$ to semiconductors$^{15,26}$ to superconductors,$^{12-14}$ and magnetic materials$^{19,20}$ as well. Also, many variants appear to adhere to the Zintl formulation of charge balance in extended solids. This chemical aspect has been investigated by several research groups.$^6,27$ Perhaps the most conspicuous aspect of clathrate materials is the guest host interaction. For example, the localized vibrational modes of the guest atoms in several clathrate compounds resonantly scatter the heat-carrying framework acoustic phonons, greatly reducing the thermal conductivity.$^1$

Most reports on clathrates thus far have concentrated on the type I structure, though in recent years other structures such as the type VIII and type IX are receiving increased attention. In general, type II clathrates have been studied far less extensively.
The impetus for the present work is the need for a better understanding of the physical properties of type II clathrates, and moreover a deeper investigation into the possible “composition space” for these materials.
An Overview of Type II Clathrates

This chapter reviews the important structural aspects of the type II clathrates, and some of the prior work that has been performed. The emphasis here is on structural and transport properties, and those aspects of the materials which can affect the electronic and thermal transport.

2.1 Structural Features

The type II clathrates crystallize with the space group $Fd\overline{3}m$ and can be depicted by the general formula $A_xE_{136}$ ($0 < x < 24$), where A has to date empirically been observed to be Na, K, Rb, Cs, or Ba and E represents Si, Ge, or Sn. The E atoms form an $sp^3$ tetrahedrally bonded framework, in which the E atoms reside at the vertices of sixteen pentagonal dodecahedra and eight hexakaidecahedra constituting the conventional unit cell (see Figure 2.1). The 136 framework atoms per conventional unit cell reside at three distinct crystallographic sites: $8a$, $32e$, and $96g$ in the Wyckoff notation. The A atoms reside inside the atomic cages formed by the polyhedra at the $8b$ (larger hexakaidecahedra) and $16c$ (smaller dodecahedra) sites. The conspicuous aspect that differentiates type II clathrates from the other structure types is the possibility of
fractionally filling the voids in type II clathrates, as seen in the formula $A_xE_{136}$. Thus type II clathrates may be synthesized such that essentially all of the voids are empty ($x = 0$), stoichiometrically filled were each site is occupied ($x = 24$), or a range of values in between. Previous work on these materials is reviewed below.

As may be seen from careful examination of the crystal structure (Figure 2.1), type II clathrates can be viewed as a derivative of the diamond crystal structure. Both structures are composed of tetrahedral $sp^3$ bonded atoms, and the clathrate structure can be thought of as an “expanded” version of the diamond structure. Typically the E-E-E bond angles range from 105° to 126° in the clathrates, and average close to the 109.5° angle that is characteristic of the diamond structure.\(^1\) However, the volume per framework atom in the clathrate is approximately 15% larger than the corresponding
diamond structure, and this is an indication of the “openness” of the clathrates. The type II clathrate structure is related to the diamond structure in another interesting way, and an alternative way to visualize the type II clathrates is to position the centers of the hexakaidecahedra at the sites of an enlarged diamond lattice. The pentagonal dodecahedra are then automatically formed in the spaces between the larger hexakaidecahedra. Thus the polyhedra share faces, filling three dimensional space.

Table 2.1 gives an idea of the relative sizes of alkali guest atoms and the cages in which they reside, taken from the work of Bobev and Sevov. From this table, a clear geometrical correlation is apparent between the relative sizes of the guest and cage, and which compounds have been experimentally observed. For example, type II clathrates with K, Rb, or Cs occupying the smaller cage have not been observed in silicon or germanium clathrates, due to these guests being too large to “fit” in the smaller dodecahedra. From the information in Table 2.1, one may also estimate the available space the guest species has to move around inside their respective cages; note that the guests inside the larger hexakaidecahedra have more “room” to move. This point will be revisited below.
Table 2.1 Comparison of ionic radii\(^a\) of the alkali metals with the approximate van der Waals radii of the empty space\(^b\) in the small (20-atom) and large (28-atom) cages in silicon and germanium type II clathrates, after Bobev and Sevov.\(^{28}\) The differences\(^c\) between cage and guest sizes are given by \(\Delta_{20}\) and \(\Delta_{28}\) for the small and large cages, respectively; negative numbers in parenthesis indicate a guest ionic radius that is larger than the cage. All values are given in angstroms.

<table>
<thead>
<tr>
<th>Guest ion</th>
<th>Ionic Radius(^a)</th>
<th>Small cage radius(^b)</th>
<th>Large cage radius(^b)</th>
<th>(\Delta_{20})(^c)</th>
<th>(\Delta_{28})(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Silicon framework</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>1.02</td>
<td>1.10</td>
<td>1.85</td>
<td>0.08</td>
<td>0.83</td>
</tr>
<tr>
<td>K</td>
<td>1.38</td>
<td>1.10</td>
<td>1.85</td>
<td>(-0.28)(^d)</td>
<td>0.47(^d)</td>
</tr>
<tr>
<td>Rb</td>
<td>1.49</td>
<td>1.10</td>
<td>1.85</td>
<td>(-0.39)(^d)</td>
<td>0.36</td>
</tr>
<tr>
<td>Cs</td>
<td>1.70</td>
<td>1.10</td>
<td>1.85</td>
<td>(-0.60)(^d)</td>
<td>0.15</td>
</tr>
<tr>
<td><strong>Germanium framework</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>1.02</td>
<td>1.25</td>
<td>2.00</td>
<td>0.23</td>
<td>0.98</td>
</tr>
<tr>
<td>K</td>
<td>1.38</td>
<td>1.25</td>
<td>2.00</td>
<td>(-0.13)(^d)</td>
<td>0.62(^d)</td>
</tr>
<tr>
<td>Rb</td>
<td>1.49</td>
<td>1.25</td>
<td>2.00</td>
<td>(-0.24)(^d)</td>
<td>0.51</td>
</tr>
<tr>
<td>Cs</td>
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<td>1.25</td>
<td>2.00</td>
<td>(-0.45)(^d)</td>
<td>0.30</td>
</tr>
</tbody>
</table>

\(^a\) Ionic radii are those calculated for various oxides, taken from Ref. 29.

\(^b\) Calculated by taking the shortest A-E distance for the respective cage, and subtracting the van der Waals radius of the E atom. Thus this is a measure of the smallest dimension of the cage.

\(^c\) \(\Delta = (\text{Cage radius}) - (\text{Ionic radius})\)

\(^d\) A guest that has not been experimentally observed at this site.

2.2 Previous Work

To date, only a very limited number of compositions have been reported for inorganic type II clathrates. In their entirety, they are: Na\(_x\)Si\(_{136}\) and Na\(_x\)Ge\(_{136}\) (0 < \(x\) < 24), and Cs\(_7\)Si\(_{136}\);\(^{11}\) Rb\(_8\)Na\(_{16}\)Si\(_{136}\), Cs\(_8\)Na\(_{16}\)Si\(_{136}\), Rb\(_8\)Na\(_{16}\)Ge\(_{136}\), and Cs\(_8\)Na\(_{16}\)Ge\(_{136}\);\(^{28}\) Ba\(_8\)Na\(_{16}\)Si\(_{136}\);\(^{30}\) Ba\(_8\)Ga\(_{32}\)Sn\(_{104}\);\(^{31}\) and Cs\(_8\)Ge\(_{136}\).\(^{32}\) A completely guest free clathrate Si\(_{136}\) was also synthesized\(^{33}\) in which essentially all of the framework cages are empty (less
than 600 pm sodium), constituting a new allotrope of elemental silicon. From this short list, it is clear that much work still remains to be done to increase the known composition space of type II clathrates, and this is a driving motivation for the present work.

As mentioned above, the pioneering studies on inorganic type II clathrates were performed by Cros et al. Clathrates with general composition \( \text{Na}_x\text{Si}_{136} \) were synthesized and characterized chemically and structurally. Compositions of \( \text{Cs}_7\text{Si}_{136} \) and \( \text{Na}_x\text{Ge}_{136} \) were also reported, but until the present work these have not been reproduced. The materials were initially of interest for their peculiar structures, but until recently little more work was carried out.

In general, type II clathrates have not been extensively studied. However, significant work has been performed on the sodium-silicon materials, \( \text{Na}_x\text{Si}_{136} \), and this system has by far been the most studied of the type II clathrates. In these materials the guest-host interaction is of prime interest, in this case the various interactions between the sodium guests and the silicon framework. Experimental investigations include powder X-ray diffraction, inelastic neutron scattering, Raman scattering, X-ray photoemission spectroscopy (XPS), extended X-ray absorption fine structure (EXAFS), electron spin resonance (ESR), nuclear magnetic resonance (NMR), magnetic measurements, and initial electrical transport measurements. Theoretical calculations have investigated the possible guest displacement, electronic and band structure, energetics, and lattice vibrational properties. It is important to note that although these materials were of the first inorganic clathrates discovered over forty years ago, until the present work their transport properties have
not been well characterized. In particular, no prior reports exist on the thermal conductivity of sodium filled Na\textsubscript{x}Si\textsubscript{136} type II clathrates.

Recently, Reny \textit{et al.}\textsuperscript{35} and Ramachandran \textit{et al.}\textsuperscript{36} independently systematically synthesized and structurally characterized the Na\textsubscript{x}Si\textsubscript{136} clathrates for a wide range of values of $x$. Rietveld refinement of the powder X-ray diffraction data for each sample was performed in both studies. As also shown in the present work, the powder diffraction patterns of the type II clathrates depend sensitively on both the guest type and content $x$. Thus refinement of the X-ray diffraction data allows a method for determining both content and relative occupancy of the cages.

### 2.2.1 Electrical Properties

In terms of scientific merit, the type II clathrates offer material systems in which the physical properties may be studied as the composition is varied in a controlled manner. As mentioned above, type II clathrates offer the ability to partially fill the crystal cages, and as is shown in the present work this has a remarkable effect on the transport properties in these materials. It was known in the initial work from Cros \textit{et al.}\textsuperscript{11} that the sodium content $x$ in Na\textsubscript{x}Si\textsubscript{136} clathrates has a significant effect on the electrical properties. The lower sodium content ($x < 11$) materials were reported to behave as semiconductors or insulators with respectable Seebeck coefficients, while the higher alkali content results in metallic behavior.$^{11,57}$
Several other researchers further investigated the Na-Si clathrates, with particular interest in the possible metal-to-insulator transition that appears to occur with composition.\textsuperscript{11,57} In analogy with alkali-doped C\textsubscript{60} fullerenes, the Na\textsubscript{x}Si\textsubscript{136} clathrates were investigated for superconductivity, but with negative results.\textsuperscript{58} Several mechanisms for both the electronic conduction and the transition from insulating to metallic behavior in Na\textsubscript{x}Si\textsubscript{136} clathrates have been suggested. Mott\textsuperscript{57} explained the transition in terms of a “Na-band,” which comes into existence as the average distance between Na guests becomes less as the content increases. Another model describes the conduction in terms of shallow impurity levels from the sodium atoms, from which electrons may be thermally excited into the framework conduction bands. Demkov \textit{et al.}\textsuperscript{51} discussed the transition in terms of a Jahn-Teller distortion with sodium filling, causing a modification of the band structure resulting in a split-off half-filled band inside of the electronic gap. It is still an open question as for exactly which value of $x$ the transition occurs, though there is agreement that it is between 8 and 12. The underlying physics of the metal-to-insulator transition and the mechanisms of conduction in Na\textsubscript{x}Si\textsubscript{136} have not been determined unequivocally.

More recently, Nolas \textit{et al.}\textsuperscript{25} have reported on the electrical and thermal properties of stoichiometric type II silicon and germanium clathrates, in which all of the cages are filled by alkali metal guests. As shown in Figure 2.2, type II clathrates such as Cs\textsubscript{8}Na\textsubscript{16}Si\textsubscript{136} and Cs\textsubscript{8}Na\textsubscript{16}Ge\textsubscript{136} possess metallic properties, such as low Seebeck coefficients and resistivities that increase with increasing temperature. These results were consistent with NMR measurements performed on Cs\textsubscript{8}Na\textsubscript{16}Si\textsubscript{136},\textsuperscript{59} Rb\textsubscript{8}Na\textsubscript{16}Si\textsubscript{136},\textsuperscript{60} and
Figure 2.2 Temperature dependence of resistivity (round symbols) and Seebeck coefficient (square symbols) for polycrystalline samples of Cs$_8$Na$_{16}$Si$_{136}$ (filled symbols) and Cs$_8$Na$_{16}$Ge$_{136}$ (open symbols). Reprinted with permission from G.S. Nolas, D.G. Vandermeer, A.P. Wilkinson, and J.L. Cohn, J. Appl. Phys. 91, 8970 (2002). Copyright 2002, American Institute of Physics.

Cs$_8$Na$_{16}$Ge$_{136}$ which also showed metallic behavior for these materials. Band structure calculations$^{32}$ indicate that the Fermi level lies clearly within the conduction band in Cs$_8$Na$_{16}$Ge$_{136}$, consistent with the above experiments.

In the initial work on the guest free clathrate Si$_{136}$, Gryko et al. reported results from resistance (see Figure 2.3) as well as optical absorption measurements. These indicated Si$_{136}$ has a wide band gap of approximately 2 eV, in good agreement with previous theoretical calculations.$^{16}$ Thus on the expansion of silicon from diamond structure to the “open” type II clathrate structure, the band gap increases by a factor of almost 2.
Very recently, we have synthesized and characterized for the first time the clathrate Cs$_8$Ge$_{136}$. The material was synthesized by controlled degassing of Na from Cs$_8$Na$_{16}$Ge$_{136}$, until essentially all of the smaller cages are empty. NMR and electrical resistivity measurements on Cs$_8$Ge$_{136}$ showed this material is also metallic, also consistent with band structure calculations performed on this material. A significant result of this work showed that Ge type II clathrates are indeed stable under partial occupation, thus offering a potential route toward tuning the electrical properties in these materials for thermoelectric applications.
2.2.2 Thermal and Vibrational Properties

As with type I clathrates, the guest-host interactions and their relation to the thermal properties is of particular interest in type II clathrates. As discussed in this section, previous work suggests that the guests in type II clathrates undergo large, anharmonic vibrations inside their atomic cages. The effects these local modes may have on the lattice thermal conductivity are therefore of prime interest.

The isotropic atomic displacement parameter (ADP or $U_{eq}$) is a measure of the mean square displacement (averaged over all directions) of an atom about its “equilibrium” site in a crystal. Using single crystal X-ray diffraction, Nolas et al.25 have measured the temperature dependence of the ADPs for stoichiometric type II Si and Ge clathrates; the results are presented in Fig. 2.4. For all four compounds, the alkali guests exhibit significantly larger ADPs than the framework atoms, and also show much stronger temperature dependencies. This is an indication that the alkali guests “rattle” in their atomic cages, corresponding to a relatively large amplitude dynamic disorder. Also note that the ADP data for the various guests also shows good qualitative agreement with the difference in sizes of guest and cage, as given in Table 2.1. Specifically, a trend is apparent that the larger the difference between cage and guest, the larger the ADP and the more pronounced the temperature dependence.

The vibrational properties of some type II clathrates have also been studied using Raman spectroscopy. Nolas et al.63 reported the Raman spectra for stoichiometric type II clathrates and for Si136, as shown in Figure 2.5. The local vibrational mode of the Cs
atom in the larger E28 cage is in fact an optic mode and is Raman active. The site symmetry at the Na atom in the smaller E20 cage results in this mode not being Raman active, thus this “rattle” mode is not present in the spectra. Clearly, the mode at approximately 50 cm$^{-1}$ can be attributed to the rattling motion of the Cs atom in its cage, as this mode is completely absent in the unfilled clathrate Si$_{136}$. 

Figure 2.4 Temperature dependent ADPs for (a) Rb$_8$Na$_{16}$Si$_{136}$, (b) Cs$_8$Na$_{16}$Si$_{136}$, (c) Rb$_8$Na$_{16}$Ge$_{136}$, and (d) Cs$_8$Na$_{16}$Ge$_{136}$, determined from single crystal X-ray diffraction. Reprinted with permission from G.S. Nolas, D.G. Vandermeer, A.P. Wilkinson, and J.L. Cohn, J. Appl. Phys. 91, 8970 (2002). Copyright 2002, American Institute of Physics.
Figure 2.5 Raman scattering spectra of Si$_{136}$ and Cs$_8$Na$_{16}$Si$_{136}$. Note that the optic mode of the Cs atom in the bottom spectrum is clearly absent in the spectra for Si$_{136}$ in which no guest atoms are present. Reprinted with permission from G.S. Nolas, C.A. Kendziora, J. Gryko, J. Dong, C.W. Myles, A. Poddar, and O.F. Sankey, J. Appl. Phys. 92, 7225 (2002). Copyright 2002, American Institute of Physics.

The frequencies of some guest atoms in type II clathrates are given in Table 2.2, as determined from ADP data,$^{25}$ Raman scattering,$^{63}$ and theoretical calculations.$^{64}$ It has been shown$^{62,65}$ that an estimate of the vibrational frequencies of weakly bonded atoms in a crystal can be extracted from ADP data by assuming a simple harmonic oscillator model to describe the guest atom’s motion. This method can also be used to estimate some of the physical properties of the material, such as the lattice thermal conductivity and Debye temperature, $\Theta_D$.$^{65}$ The frequencies in the table agree qualitatively, and all are
Table 2.2 Rattler frequencies in cm\(^{-1}\) as determined from Raman scattering,\(^{63}\) ADPs from single crystal XRD,\(^{25}\) and theoretical calculations.\(^{63,64}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cs or Rb</th>
<th>Na</th>
<th>Cs or Rb</th>
<th>Na</th>
<th>Cs or Rb</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ADP</td>
<td>Raman</td>
<td>Theory</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs(<em>8)Na(</em>{16})Si(_{136})</td>
<td>53.4</td>
<td>141</td>
<td>57</td>
<td>---</td>
<td>64</td>
<td>120</td>
</tr>
<tr>
<td>Rb(<em>8)Na(</em>{16})Si(_{136})</td>
<td>55.0</td>
<td>130</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Cs(<em>8)Na(</em>{16})Ge(_{136})</td>
<td>41.8</td>
<td>117</td>
<td>18</td>
<td>---</td>
<td>21</td>
<td>89</td>
</tr>
<tr>
<td>Rb(<em>8)Na(</em>{16})Ge(_{136})</td>
<td>42.9</td>
<td>127</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Quite low. Indeed, theoretical calculations\(^{64}\) of phonon dispersion show that the “rattler” modes cut the acoustic phonon branches, indicating the possibility for strong interaction between the guest and framework vibrations.

Recently, the thermal conductivities of some type II clathrates have been reported.\(^{25,66,67}\) The results for the unfilled silicon clathrate Si\(_{136}\) and completely filled Cs\(_8\)Na\(_{16}\)Si\(_{136}\) are compared in Figure 2.6. The empty clathrate Si\(_{136}\) has a remarkably low thermal conductivity, almost 30 times lower than elemental diamond-structured silicon at room temperature, and approaches that of amorphous SiO\(_2\) (a-SiO\(_2\); glass). This result is consistent with a theoretical calculation of the thermal conductivity of an unfilled type I clathrate Ge\(_{46}\), which showed an order of magnitude decrease as compared to diamond structured germanium. Because Si\(_{136}\) is essentially an electrical insulator,\(^{17}\) thermal conduction in this material is almost entirely due to the lattice contribution. The notable aspect of this result is that the thermal conductivity is low even in the absence of “rattler” atoms inside the cages, where the resonant phonon scattering mechanism present in some type I clathrates is absent in Si\(_{136}\). The stoichiometric Cs\(_8\)Na\(_{16}\)Si\(_{136}\) has a relatively higher
thermal conductivity, which can be attributed to the large electronic contribution due to the metallic properties of this material. However, using the approach described by Sales et al., Nolas et al. estimated from the ADP data that the room temperature lattice thermal conductivity of Cs$_8$Na$_{16}$Si$_{136}$ to be on the order of 2 W/m-K.
2.3 Applications

In addition to the interesting physics that can be learned from type II clathrates, these materials hold promise for a number of applications. One of the reasons for the recent surge in interest in clathrates is due to the discovery of superconductivity in some clathrate materials. The first report was for the type I clathrate Ba$_2$Na$_6$Si$_{46}$,\textsuperscript{12} and further reports soon followed. These materials are unique in that they are covalently bonded superconductors. Investigations into superconductivity in type II clathrates have thus far produced negative results.\textsuperscript{58} However, if found superconducting type II clathrates could offer a useful system for studying the effects of the guest content on the superconducting state, since the former may be varied in these materials.

Type II clathrate materials are also of interest for several potential applications involving the solid state conversion of energy. For example, these materials are raising continued interest in the field of thermoelectrics,\textsuperscript{68} which is the conversion of electrical energy to thermal energy, and vice versa. For certain materials, imposing a temperature gradient across the material induces a corresponding electrical voltage. Under open circuit and linear response conditions, this voltage $\Delta V$ is simply proportional to the temperature difference, so that

$$\Delta V = S \Delta T,$$

where $S$ is a bulk material property known as the Seebeck coefficient or thermopower, and
\( \Delta T \) is the imposing temperature difference across the material. This most basic thermoelectric effect is known as the Seebeck effect, and by convention the sign of \( S \) is negative (positive) if the majority carriers are electrons (holes). In metals, the simplest picture \(^6^9\) of the Seebeck effect can be described in terms of the differing thermal velocity distributions of charge carriers at the hot and cold ends, in the steady state resulting in an accumulation of net charge at the cold end and an accompanying potential difference typically on the order of a few up to tens of \( \mu V \) for a \( \Delta T \) of 1 K. The effect is significantly larger in semiconductors, \(^6^9\) due to the fact that in addition to the differing thermal velocity distributions, the Fermi-Dirac distributions at the hot and cold ends may also be appreciably different, thus additionally causing varying carrier excitation with position. Thus semiconductors typically have Seebeck coefficients of a few hundred to a few thousand \( \mu V/K \).

The usefulness of a thermoelectric material is given by its dimensionless figure of merit \( ZT \), where

\[
ZT = \frac{S^2 \sigma}{\kappa} T. \tag{2.2}
\]

Here \( \sigma \) is the electrical conductivity, \( \kappa \) is the total thermal conductivity (\( \kappa = \kappa_e + \kappa_L \), the sum of the electronic and lattice contributions, respectively), and \( T \) is the absolute temperature. The Seebeck effect can be used to generate power, converting the energy from a heat source into electrical current when a thermoelectric circuit is connected to a load. Figure 2.7 shows a schematic of a thermoelectric couple, in which n-type and p-
Figure 2.7 Schematic of a thermoelectric couple designed for power generation. Reprinted with permission from Ref. 70.

Type materials are connected electrically in series and thermally in parallel, and a load is connected to the circuit. The imposing temperature difference causes a current to flow in the circuit, thus generating power.

Currently, state of the art thermoelectric materials for power generation have $ZT$ on the order of or less than 1, resulting in efficiencies for thermoelectric power generation that are less than 30% of the Carnot limit. Thus power generation using thermoelectric technology has been limited to niche applications, or in situations where reliability and longevity outweigh efficiency and performance. An example is the case of
Radioisotope Thermoelectric Generators (RTGs) that provide the onboard power for NASA deep space probes such as Voyager or Cassini.

Within the past two decades there has been much renewed interest in thermoelectric materials research. One reason for this is Slack’s concept of the ideal “Phonon Glass Electron Crystal” (PGEC) material. From Eq. (2.1), it is clear that a good thermoelectric material must simultaneously possess good electrical properties (i.e. high electrical conductivity and Seebeck coefficient) and low thermal conductivity. Thus Slack proposed the design or discovery of materials that would conduct heat like a structural glass (“Phonon Glass”) yet conduct electricity as in a high quality single crystal semiconductor (“Electron Crystal”). In particular, Slack suggested that clathrate materials may fulfill the requirements of a PGEC, and investigations by Nolas et al. among others have shown this approach to be valid in the search for new thermoelectric materials. In addition to the good semiconducting properties that some clathrates possess, several variants have been shown to have very low thermal conductivities and in a few cases literally “glasslike.” The low thermal conductivity of these materials has been attributed to the resonant scattering of the heat carrying framework acoustic phonons by the localized vibration modes of the guest atoms.

As discussed above, type II clathrates possess many similar properties as type I clathrates, in particular the guest atoms in type II clathrates also display large anharmonic motion inside of their cages. The lattice thermal conductivities of type II clathrates are in general expected to be quite low. In addition, the ability to partially fill the cages in type II clathrates allows for an additional control for simultaneously tuning all of the transport
properties in these materials. A deeper understanding of the transport properties in type II clathrates is needed in order to assess the potential these materials hold for thermoelectric applications.

Another potential application for type II clathrates is for photovoltaics, or the direct conversion of light to electricity. Technologies such as photovoltaics are currently attracting much attention as candidates to fulfill the world’s increasing energy needs. However, currently the relatively low efficiency and high fabrication costs of solar cells form a barrier preventing photovoltaics from significantly contributing to global energy production. Figure 2.8 shows a simplified band diagram schematic of a conventional p-n homojunction used for photovoltaic conversion of light into electricity. Typically, production level solar cells have used a silicon p-n junction design, which has been shown to have a 31% maximum energy conversion efficiency.76

Figure 2.8 Band diagram schematic of carrier generation in a p-n homojunction. The built-in electric field caused by the p-n junction allows for separation of photo-generated electrons (e⁻) and holes (h⁺).
Commentary on the present status and future of photovoltaic technology has led to the classification of first, second, and third generation PV materials. First generation PV technology is based on single crystal and polycrystalline silicon wafer devices. Second generation PV cells use thin film technology and include CdS/CdTe and amorphous Si/SiGe or Si/H materials. The proposal for third generation PV materials includes finding (a) new approaches that dramatically increase the efficiency of devices, via material mechanisms that are not limited to the 31% target efficiency of a single junction device, and (b) development of technologies and materials possessing moderate efficiencies but at a drastically reduced cost. Success in either or both of these areas could enable photovoltaics to become a feasible large-scale energy conversion technology.

Type II clathrates first attracted attention for photovoltaic and optoelectronic applications upon the theoretical prediction and experimental confirmation that the type II clathrate Si\(_{136}\) is a wide 2 eV band gap insulator, corresponding to absorption in the visible part of the electromagnetic spectrum. As Si\(_{136}\) is a silicon-based material, type II silicon clathrates could be integrated into currently used silicon technology. Moreover, theoretical calculations by Moriguchi et al. show that alloyed Si\(_{136-x}\)Ge\(_{x}\) clathrates possess direct band gaps in the range 1.2 to 2.0 eV. Na\(_{x}\)Si\(_{136}\) clathrates have also been investigated in hopes of finding potential intermediate band materials, an approach directed towards finding materials that are not constrained to the Shockley-Queisser 31% limit. The present work is part of an ongoing effort of experimentally investigating the merit of type II clathrates for the above technological applications.
3

Synthesis and Sample Preparation

3.1 Degassing of Silicides and Germanides

One route to the synthesis of type II clathrates is through the controlled vacuum
decomposition known as “degassing” of alkali or alkaline earth silicides and germanides.
Several silicides and germanides were investigated in the present work, the synthesis
results of which are presented in this section.

3.1.1 Preparation of Na$_x$Si$_{136}$ clathrates

The Na$_x$Si$_{136}$ specimens produced in this work were synthesized using a multi-
step process, based on a modified procedure compared to what has been previously
reported in the literature.$^{11}$ First, high purity sodium metal (Alfa Aesar, 99.95%) and
silicon powder (High Purity Chemicals, 99.999%) were combined in the ratio 1:(1 + $\delta$)
silicon to sodium, where $\delta \sim 0.05$ to 0.2. The additional Na metal ensures the complete
reaction of the silicon and compensates for the high vapor pressure of Na at elevated
temperatures. The product is the Zintl compound NaSi (see Figure 3.1), with an excess of
sodium. NaSi is very reactive in air and moisture, thus all handling of the materials was
Figure 3.1 Crystal structure of the Zintl phase NaSi, emphasizing the Si$_4^-$ cluster units (blue) and Na$^+$ ions (orange). The monoclinic unit cell is outlined.

carried out in a nitrogen-filled glove box (VAC Atmospheres NEXUS System) with oxygen levels less than 5 ppm. All NaSi products were analyzed using powder X-ray diffraction (Rigaku MiniFlex and Bruker-Axs D8 Focus) and the diffraction patterns compared to those in the literature$^82$ to ensure the NaSi structure had formed and to verify the absence of unreacted elemental silicon. The silicides were sealed under nitrogen on a glass plate sample holder by thin plastic sealed with vacuum grease, to avoid decomposition during X-ray diffraction measurements.

In the next step, small portions (~ 250 mg) of NaSi were ground to very fine powders inside of the nitrogen-filled glove box. The powder was placed into fused quartz boats, and then into a $\frac{3}{4}$ inch diameter fused quartz tube that was sealed on one end and open at the other, the quartz boat with sample being placed at the sealed end. All quartz tubes and boats were fabricated onsite in the Novel Materials Laboratory. A vacuum
coupling and valve was then attached to the open end of the tube and the valve closed to ensure that the sample volume remained under a nitrogen atmosphere during the process of removal from the glove box and attaching to the vacuum system. Upon attaching to the vacuum system, the line was first evacuated and then the coupling valve opened to avoid the sample coming in contact with air. A schematic of the custom-designed vacuum furnace apparatus is shown in Figure 3.2.

Upon reaching a vacuum of $10^{-5}$ to $10^{-6}$ torr, the tube and sample were inserted into a tube furnace, preheated to approximately 275°C. A thermocouple was placed alongside the tube to measure the furnace temperature at the position of the sample continuously throughout the synthesis process. Heating the NaSi at 275°C for approximately 12 hours evaporated excess Na metal from the sample, which in turn
condensed on the inside of the quartz tube outside of the furnace. A small “test tube” was also placed in this region to minimize any sodium vapor entering the vacuum line.

After being held at 275°C, the sample was then slowly heated to a temperature between 410 and 430°C at an average rate of 1-2°C/min. As seen in Fig. 3.1, the structure of NaSi consists of Na⁺ ions coordinated with tetrahedral Si₄⁻ units. As the temperature is increased, the sodium ions are “evaporated” from the structure, likely as a neutral species, presumably causing the Si clusters to “close in” on the remaining Na ions forming the clathrate structures. The evaporated Na is allowed to condense on the inside of the tube, in the region outside of the furnace. Using the above procedure, samples with nominal compositions Na₁Si₁₃₆, Na₈Si₁₃₆, Na₁₂Si₁₃₆, and Na₁₆Si₁₃₆ were synthesized. The synthetic products are very fine bluish powders, and the clathrates are stable in air, moisture, and strong acids (excluding hydrofluoric acid).

As is well known to those skilled in the synthesis of Na-Si clathrates, the type II structure is not the only possible product resulting from the above procedure. In fact, the type I clathrate Na₈Si₄₆ is also commonly found as an impurity and it has been quite difficult to avoid forming this phase. Previous authors have reported the type I phase constituting as much as 50% by weight of the synthesis products. Inasmuch as Na₈Si₄₆ and NaₓSi₁₃₆ have different densities, Ramachandran et al. were able to reduce the percent of the former in their samples to between 1 and 10%, using a density separation technique. In the present work, we have achieved a much higher purity of the type II NaₓSi₁₃₆ “as synthesized” than previously reported, without the need for additional separation techniques. Although all of the specific synthesis details were not given in the
previous works, we can hypothesize some of the reasons that have led to better results in this study. Great care was taken to grind the NaSi to very fine powders before degassing, and this appears to increase the fraction of the $\text{Na}_x\text{Si}_{136}$ phase. Also, in general higher yield of $\text{Na}_x\text{Si}_{136}$ was obtained by slowly heating the silicide to the synthesis temperature, though this is in contrast to the results of Gryko\textsuperscript{83} who found that “flash-degassing” using rapid heating rates minimizes the $\text{Na}_8\text{Si}_{46}$ fraction. Theoretical calculations\textsuperscript{16,53} of the total energy predict that the $\text{Na}_x\text{Si}_{136}$ structure is slightly more thermodynamically stable (lower total energy) than the $\text{Na}_8\text{Si}_{46}$ structure, thus a slower rate of heating could allow the former to form in higher yield. Generally better results were also achieved in the present study by using smaller amounts of starting material.

Initial microprobe analysis indicated a significant presence of oxygen (> 5 wt%) in our $\text{Na}_x\text{Si}_{136}$ specimens. Therefore, a procedure was employed for all samples in which the powders where first washed with a 5 M aqueous solution of hydrochloric acid, then washed with distilled water, and finally washed with ethanol and then dried under vacuum. The procedure was carried out inside a nitrogen-filled glove bag, and all liquids were bubbled with high purity nitrogen gas prior to washing in order to remove oxygen dissolved in the liquids. This procedure produced samples with greatly reduced oxygen content (< 1 wt%).

After the acid washing procedure, the powder $\text{Na}_x\text{Si}_{136}$ specimens were further ground using an alumina mortar and pestle in an inert nitrogen atmosphere, and then densified by hot-pressing at 220$^\circ$C and 5 kbar for 12 hours. This produced specimens with densities of approximately 70% of the theoretical X-ray density. We note that this
density is rather low, resulting from the challenge posed in the densification of silicon-based clathrates. Methods of obtaining higher density, such as spark plasma sintering (SPS), are currently being investigated.

### 3.1.2 Preparation of $\text{Na}_x\text{Ge}_{136}$ clathrates and the new phase $\text{Na}_{1-x}\text{Ge}_3$

An extensive and systematic investigation into the synthesis of $\text{Na}_x\text{Ge}_{136}$ was also undertaken. The synthesis methods were essentially those explained above for $\text{Na}_x\text{Si}_{136}$, but using the Zintl phase $\text{NaGe}$ as starting material. The results of the investigation are qualitatively summarized in Figure 3.3, which shows the relative percentages of various products observed in the powder X-ray diffraction (XRD) patterns, determined from the

![Figure 3.3](image)

**Figure 3.3** Qualitative representation of phase percentages from products obtained from thermal decomposition of $\text{NaGe}$. 

31
relative intensities of the diffraction peaks in the individual spectra. The figure was
compiled from the XRD spectra of more than two dozen separate samples. As shown in
the figure, the type II clathrate Na$_x$Ge$_{136}$ was found to form in the range of 350 to 370°C,
but the yield was very low. Thus production of large enough pure samples for further
characterization was not possible. However, over a broader range of temperature an
initially unidentifiable Na-Ge phase was found to be the dominant synthesis product. As
discussed in Section 4.5, as a part of this work the crystal structure of the unknown phase
has been solved and its composition was determined to be Na$_{1.5}$Ge$_3$ ($0 < x < 1$). This
constitutes the discovery of a new binary compound in the Na-Ge system.

3.1.3 Other Silicides and Germanides

In the course of this work, several other silicides and germanides were
investigated, however none produced type II clathrates in the high yield as found with
NaSi. As discussed in Section 2.1, there appears to be relative size constraints between
guest and framework polyhedra that limit the formation of the clathrates (see Table 2.1).
Upon further analysis of our results, combined with those in the literature, there appears
also to be correlation between the starting structures of the silicides and germanides and
the products that are formed upon their thermal decomposition. One common
characteristic of all silicides (germanides) that decompose to produce clathrates is the
presence of Si$_4^{4-}$ (Ge$_4^{4-}$) clusters, which are coordinated with alkali or alkaline earth ions.
Presumably, upon degassing of the alkali or alkaline earth atoms these clusters reorganize
and connect to form the frameworks of the clathrate compounds. Thus, empirically the presence of these four-atom clusters seems to be necessary for formation of the four-bonded clathrate frameworks using the controlled vacuum decomposition technique.

Table 3.1 presents the structures of a variety of silicides and germanides and the products that are obtained upon their thermal decomposition under vacuum, compiled from the present work and from the literature. Most of the starting materials are

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space Group</th>
<th>Lattice</th>
<th>Structural Isotype</th>
<th>Decomposition Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaSi</td>
<td>$C2/c^{84}$</td>
<td>monoclinic</td>
<td>NaSi</td>
<td>$Na_xSi_{136}$, $Na_8Si_{46}$</td>
</tr>
<tr>
<td>KSi</td>
<td>$P4_3n^{85}$</td>
<td>cubic</td>
<td>KSi</td>
<td>$K_8Si_{46}$</td>
</tr>
<tr>
<td>RbSi</td>
<td>$P4_3n^{85}$</td>
<td>cubic</td>
<td>KSi</td>
<td>$Rb_{8-x}Si_{46}$</td>
</tr>
<tr>
<td>CsSi</td>
<td>$P4_3n^{85}$</td>
<td>cubic</td>
<td>KSi</td>
<td>$Cs_xSi_{136}$</td>
</tr>
<tr>
<td>NaGe</td>
<td>$P2_1/c^{84}$</td>
<td>monoclinic</td>
<td>NaGe</td>
<td>$Na_xGe_{136}$, $Na_{1-x}Ge_{3}$</td>
</tr>
<tr>
<td>KGe</td>
<td>$P4_3n^{85}$</td>
<td>cubic</td>
<td>KSi</td>
<td>$K_8Ge_{46-δ}$</td>
</tr>
<tr>
<td>RbGe</td>
<td>$P4_3n^{85}$</td>
<td>cubic</td>
<td>KSi</td>
<td>$Rb_{8}Ge_{46-δ}$</td>
</tr>
<tr>
<td>NaKGe$_2$</td>
<td>$P4_3n^{85}$</td>
<td>cubic</td>
<td>KSi</td>
<td>$Na_xK_2Ge_{136}$, $Na,K_2Ge_{46-δ}$</td>
</tr>
<tr>
<td>NaRbGe$_2$</td>
<td>$P4_3n^{85}$</td>
<td>cubic</td>
<td>KSi</td>
<td>$Na_xRb_xGe_{46-δ}$</td>
</tr>
<tr>
<td>NaRbSi$_2$</td>
<td>unknown</td>
<td>unknown</td>
<td>unknown</td>
<td>$Rb_8Na_{16}Si_{136}$</td>
</tr>
<tr>
<td>NaCsSi$_2$</td>
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<td>unknown</td>
<td>unknown</td>
<td>$Cs_8Na_{16}Si_{136}$</td>
</tr>
<tr>
<td>BaNa$_2$Si$_4$</td>
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<td>monoclinic</td>
<td>unknown</td>
<td>$Na_xBa_6Si_{46}$, $Ba_8Na_{16}Si_{136}$</td>
</tr>
<tr>
<td>BaNa$_2$Ge$_4$</td>
<td>unknown</td>
<td>unknown</td>
<td>unknown</td>
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</tbody>
</table>
cubic, and result in type I clathrate as the majority phase. Overall, the only starting material found to produce type II clathrate in high yield is NaSi. Note that none of the other silicides or germanides listed in this table shares the NaSi crystal structure, though NaGe is monoclinic but with different space group symmetry. This tabulation suggests that the design or discovery of starting materials with the desired structures may be an appropriate approach for the synthesis of type II silicon and germanium clathrates using the Zintl phase decomposition method. We also note that several of the clathrate compositions, including $\text{Na}_x\text{K}_y\text{Ge}_{46-\delta}$, $\text{Na}_x\text{Rb}_y\text{Ge}_{46-\delta}$, and $\text{Na}_x\text{K}_y\text{Ge}_{136}$, were previously unreported.

### 3.2 Direct Synthesis of Cs$_8$Na$_{16}M_y\text{Ge}_{136-y}$ Clathrates ($M = \text{Ag, Cu}$)

It was recently shown$^{28}$ that type II clathrates can also be synthesized by direct reaction of the elements. For the first time, we have synthesized in the present work type II germanium clathrates in which the framework germanium atoms are substituted by other species, specifically transition metal elements. This shows that type II clathrates are stable under framework substitution, opening new doors to synthesis of novel type II clathrates. In particular, this proves the ability to “dope” these compounds with other atomic species, which holds promise for control of the electronic properties of type II clathrates.

A series of silver and copper substituted samples was synthesized by the direct reaction of high purity Na (99.95%, Alfa Aesar), Cs (99.98%, Alfa Aesar), Ge (99.999%,...
High Purity Elements), and Ag (99.9%, Alfa Aesar) or Cu (99.9%, Alfa Aesar).

Stoichiometric amounts of the elements were combined in tungsten crucibles and sealed in steel canisters (see Figure 3.4) under nitrogen atmosphere. The steel canisters were in turn sealed inside quartz ampoules. The mixtures were held at 800°C for 2 days, slowly cooled to 650°C, and then held at this temperature for 7 days. The samples were then allowed to cool to room temperature; the synthesis schedule is shown in Figure 3.4. We note that the use of tungsten crucibles as opposed to niobium avoids reaction of the crucible with germanium, allowing for a higher synthesis temperature and thus approximately one-third the synthesis time (nine days as opposed to three to four weeks) as previously reported in the synthesis of stoichiometric type II germanium clathrates.25,28

Figure 3.4 Temperature schedule for the synthesis of the framework substituted type II germanium clathrates.
Using this procedure, series of $\text{Cs}_8\text{Na}_{16}\text{Cu}_y\text{Ge}_{136-y}$ ($y = 2.667, 3.14, 5, 8, 10, 16$) and $\text{Cs}_8\text{Na}_{16}\text{Ag}_y\text{Ge}_{136-y}$ ($y = 2.667, 5, 8$) clathrates were synthesized. Here Cs atoms occupy the larger hexacaidecahedra and Na atoms occupy the smaller dodecahedra, and the transition metals substitute for the Ge atoms on the framework. The products generally consist of coarsely grained crystalline powders along with some larger crystals (see Figure 3.5), and are stable in air and moisture. Cu substituted samples with $y = 5$ and 8 were ground to 325 mesh and hot pressed at 400°C into pellets of approximately 80% of the theoretical X-ray density. From X-ray diffraction, no structural transformation of these samples was detected after hot-pressing.

**Figure 3.5** Small clusters of as-grown crystallites of $\text{Cs}_8\text{Na}_{16}\text{Cu}_y\text{Ge}_{136-y}$ clathrates.


3.3 Partially Filled Type II Germanium Clathrates

As mentioned in Section 2.2, recently we have reported for the first time on the synthesis of partially filled type II clathrate Cs$_8$Ge$_{136}$.$^{32}$ Although the type I germanium clathrates are found to be much less stable with respect to partial filling,$^8$ type II clathrates can be synthesized with the framework polyhedra partially occupied.

Other type II germanium clathrates can also be synthesized with partial occupation. In the present work, a partially occupied Na$_x$Rb$_8$Ge$_{136}$ clathrate was produced. First, a “fully loaded” Rb$_8$Na$_{16}$Ge$_{136}$ clathrate was synthesized. Stoichiometric amounts of high purity Na, Rb, and Ge were combined in a tungsten crucible, and the reaction of the constituents carried out in a similar manner as in the metal substituted clathrates above. The resulting Rb$_8$Na$_{16}$Ge$_{136}$ clathrate was then ground to very fine powder, and degassed under high vacuum at a temperature of 310°C for 24 hours, using the apparatus shown in Figure 3.2. The sample was then reground under nitrogen, degassed again at increased temperature of 320°C. This process was repeated, each time increasing the temperature by 10 to 15°C, resulting in the degassing of Na from the structure. As shown in Figure 3.6, as the degassing procedure progressed the lattice parameter showed a decrease, corresponding to a slight shrinking of the structure on removal of the Na guests. Also, from the inset of Figure 3.6 it is clear that the structure is stable with respect to partial occupation of the voids, as was also found in the case of Cs$_8$Ge$_{136}$.$^{32}$ These results reveal yet another avenue that can be explored in synthesizing novel type II clathrates, and also may offer a way to control the physical properties of these materials.
Figure 3.6 Lattice parameter of Na$_x$Rb$_8$Ge$_{136}$, as measured after vacuum degassing at the indicated temperature. Open and closed circles indicate results from the present work on two different samples, while the open triangle is from the work of Gryko (unpublished). The inset shows that the integrity of the clathrate framework is maintained after the procedure; an “*” indicates an internal NIST silicon standard, used to calibrate the peak positions.
Structural and Chemical Characterization

4.1 Characterization of \( \text{Na}_x\text{Si}_{136} \) Clathrates

In has been shown previously\textsuperscript{35,36} that the X-ray diffraction (XRD) spectra of \( \text{Na}_x\text{Si}_{136} \) clathrates are highly dependent on the Na content \( x \). This is illustrated in Figure 4.1, which shows simulated theoretical powder XRD spectra for \( \text{Na}_x\text{Si}_{136} \) clathrates, as a function of the sodium content \( x \). These theoretical spectra were calculated by inputting \( \text{Na}_x\text{Si}_{136} \) structural details into the crystallography software PowderCell.\textsuperscript{88} Note that the relative intensities of the Bragg peaks display a clear dependence on the Na content, especially for the (311), (222), (511), and (531) reflections. This allows for the guest content of samples to be determined quantitatively via refinement of experimental XRD data. Furthermore, the relative intensities are also dependent upon the relative occupancy of the two distinct polyhedron sites.

We have employed the Generalized Structure Analysis Software\textsuperscript{89} (GSAS) suite as well as the PowderCell\textsuperscript{88} computer program to perform Rietveld analysis and refinement on the \( \text{Na}_x\text{Si}_{136} \) specimens in this study. The principle behind Rietveld analysis\textsuperscript{90} is to perform a non-linear least squares fit to experimental diffraction data using a structural model. Structural (i.e. lattice parameters, atomic positions, etc.) and instrumental (i.e. peak shape, profile coefficients, zero shift, etc.) parameters may all be
Figure 4.1 Simulated theoretical X-ray diffraction patterns for Na$_x$Si$_{136}$ clathrates as a function of the Na content $x$, calculated using the PowderCell computer software. The lattice parameters were kept constant for all compositions, and the 8$b$ (larger cage) site was filled first as $x$ was increased.
refined, in order to determine the structural details of the sample under investigation. Since the diffraction patterns of Na$_x$Si$_{136}$ clathrates depend sensitively on the guest atom content, refinement of the X-ray diffraction data allows for the determination of the guest concentration.

As noted in Section 3.1.1, high purity Na$_x$Si$_{136}$ samples were synthesized with nominal Na contents of $x = 1, 8, 12, \text{ and } 16$. Type II sodium-silicon clathrates with $x = 1$ and 8 were characterized in more detail. Figures 4.2 and 4.3 show typical refined powder diffraction patterns for Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$, respectively. The compositions determined from refinement of the X-ray diffraction data were in turn corroborated from Energy Dispersive X-ray Spectroscopy (EDS) performed by Dr. Jan Gryko at Jacksonville State

![Figure 4.2](image)

**Figure 4.2** Refinement of powder XRD data for Na$_1$Si$_{136}$. Peaks associated with Na$_8$Si$_{46}$ and diamond-structure silicon are indicated by arrows.
Figure 4.3 GSAS fit of the powder XRD data for Na₈Si₁₃₆. The peak at approximately 33 degrees is due to the presence of a small amount (~ 5 wt%) of Na₈Si₄₆ in the sample. Data collected and fit by Dr. Jan Gryko, Jacksonville State University.

Table 4.1 Structure and composition of Na₁Si₁₃₆ and Na₈Si₁₃₆. Compositions are given as determined from EDS and XRD refinement. Grain size was determined from optical micrographs taken on polished densified samples, according to ASTM Standard E112-88

<table>
<thead>
<tr>
<th>Sample Nominal Composition</th>
<th>Composition From EDS</th>
<th>Composition From XRD</th>
<th>Average Grain Size (µm)</th>
<th>Approximate wt% of Na₈Si₄₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₁Si₁₃₆</td>
<td>Na₁.₇Si₁₃₆</td>
<td>Na₀.₆Si₁₃₆</td>
<td>4.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Na₈Si₁₃₆</td>
<td>Na₈.₄Si₁₃₆</td>
<td>Na₈.₈Si₁₃₆</td>
<td>3.1</td>
<td>5.0</td>
</tr>
</tbody>
</table>
University. Some structural and compositional details for the Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$ samples are given in Table 4.1.

One very useful method for characterization of the vibrational properties of materials is Raman scattering spectroscopy. The Raman effect is due to the inelastic scattering of light from a material, corresponding to the gain or loss of energy in the material such as in the creation or annihilation of phonons. As shown in Figure 4.4, Raman spectra were collected for Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$ by Dr. Chris Kendziora at the Naval Research Laboratory in Washington, D.C. The figure shows Stokes Raman scattering spectra for the two samples in both parallel (VV) and perpendicular (HV) polarization.

![Stokes Raman scattering spectra for Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$](image)

**Figure 4.4** Stokes Raman scattering spectra for Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$. VV indicates parallel polarization, HV indicates perpendicular polarization. The arrows indicate the Si$_{136}$ framework modes.
polarizations using a 647 nm laser line. Also shown are data for Na$_8$Si$_{136}$ using 514 nm laser light. The arrows in the figure indicate the Raman active silicon framework modes, as determined in a prior work,$^{63}$ and these spectra are a testament to the high quality of the Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$ samples.

To investigate the stability of type II silicon clathrates, differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q600, under flowing nitrogen gas at a pressure of 1 atm., in the range 100 to 800$^\circ$C. Figure 4.5 shows heat flow as a function of temperature for Na$_x$Si$_{136}$ samples with $x = 0, 1, 8$. The Na$_8$Si$_{136}$ clathrates are stable until slightly above 600$^\circ$C, at which point exothermic decomposition to diamond structure silicon occurs, as verified by post-DSC XRD. The

Figure 4.5 Heat flow as a function of temperature for Na$_x$Si$_{136}$ samples with $x = 0, 1, 8$. 
fact that decomposition is exothermic agrees qualitatively with theoretical calculations that predict the type II silicon framework to be slightly higher in energy than the ground state of diamond structure silicon.\textsuperscript{16} It is interesting to note that at synthesis temperatures (under vacuum of \( \sim 10^{-6} \) torr) in excess of 450\(^\circ\)C, diamond-structure silicon becomes an increasingly larger and eventually total percentage of the synthesis products. Thus clearly the stability of these materials is dependent on pressure. The relatively high decomposition temperature of the type II silicon clathrates indicates these materials may hold promise for applications at elevated temperatures.

4.2 Characterization of Cs\(_8\)Na\(_{16}\)M\(_y\)Ge\(_{136-y}\) Clathrates (M = Ag, Cu)

The type II germanium clathrates synthesized in this study constitute the first framework substituted type II clathrates synthesized to date, with the single exception of the report of Ba\(_{16}\)Ga\(_{32}\)Sn\(_{104}\) which was rather described as a Zintl compound.\textsuperscript{30} 

The results from the initial powder X-ray diffraction measurements (Rigaku MiniFlex diffractometer) for the type II germanium clathrates are shown in Figure 4.6 (Ag-substituted) and Figure 4.7 (Cu-substituted). From the diffraction patterns, the samples all appear essentially single-phase, with the exception of an occasional very weak peak at approximately 27 degrees 2\(\theta\) attributed to a trace amount of unreacted elemental germanium. The NIST 640c internal silicon standard (peaks indicated by a “*” in the bottom spectra of both figures) was added to the samples for XRD in order to correct the peak positions for possible sample displacement and instrumental factors in
calculation of lattice parameters. As seen in Figure 4.8, the lattice parameters of the Ag-substituted type II germanium clathrates increased with substitution, while those for the Cu-substituted samples decreased. The latter results are consistent with previous reports on Cu-substituted type I germanium clathrates, which also showed a decrease in lattice parameter.\textsuperscript{91} For both Ag and Cu samples, the leveling out of the lattice parameter with

![Figure 4.6 Powder XRD patterns for Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$ clathrates. An “*” indicates a peak due to the NIST internal silicon standard used to calibrate the spectra, which is present in all patterns for 2theta corrections used in the calculation of lattice parameters.](image-url)
Figure 4.7 Powder XRD patterns for Cs₈Na₁₆Cu₇₂Ge₁₃₆₋ₙ clathrates. The “*” indicates a NIST internal silicon standard used to calibrate the spectra, which is present in all patterns for 2theta corrections used in the calculation of lattice parameters.
Figure 4.8 Lattice parameter as a function of transition metal content for the Cs$_8$Na$_{16}$Cu$_y$Ge$_{136-y}$ (closed circles) and Cs$_8$Na$_{16}$Ag$_y$Ge$_{136-y}$ (open triangles) clathrates. The Ag-substituted clathrates showed an increase in lattice parameter, while the Cu-substituted samples showed a decrease. The leveling out of the lattice parameters may indicate a solubility limit has been reached.

doping concentration indicates that a solubility limit may have been reached for transition metal substitution, occurring at $y \sim 3$ for Ag and $y \sim 8$ for Cu.

Transport properties were measured on Cu substituted samples with $y = 5$ and 8. Energy dispersive X-ray spectroscopy indicated average compositions of Cs$_{10.2}$Na$_{16.2}$Cu$_{4.7}$Ge$_{131.3}$ and Cs$_{9.1}$Na$_{14.4}$Cu$_{7.7}$Ge$_{128.3}$ for these two samples, respectively. Hereafter, these samples will be referred to as Cs$_8$Na$_{16}$Cu$_5$Ge$_{131}$ and Cs$_8$Na$_{16}$Cu$_8$Ge$_{128}$.
4.3 The New Compound Na$_{1-x}$Ge$_3$

As discussed in Section 3.2, an extensive investigation into the synthesis of Na-Ge type II clathrates resulted predominantly in an unidentifiable Na-Ge phase. In order to identify this dominant phase, we initially turned to the literature. However, we found conflicting reports. Several binary compounds have been reported for the Na-Ge system, including NaGe, $^{84,85}$ Na$_{12}$Ge$_{17}$, $^{92}$ Na$_3$Ge, $^{93}$ and NaGe$_4$. $^{94}$ Some of these reports, in particular for “NaGe$_{4}$” $^{94}$ were disputed by other authors, $^{95}$ who suggested instead that the compound was in fact Ge or even a clathrate phase. $^{95,96}$ Upon comparing our powder X-ray diffraction data to the available literature and diffraction databases, the question of the composition and structure of our unknown phase remained. Thus, in order to help clarify the confusion in the literature and perhaps better understand the route to synthesis of Na-Ge type II clathrates, we have further characterized this phase.

Using synchrotron X-ray diffraction experiments performed on approximately 600 mg of material, Dr. James Kaduk of Innovene and Dr. Winnie Wong-Ng of NIST used a Monte Carlo simulation technique $^{97}$ in order to solve the structure of the unknown phase. The structure was then refined by the Rietveld method $^{90}$ using the GSAS software suite. $^{89}$ From these results, we present a preliminary structural model for this new material. The structure was indexed to a hexagonal unit cell with space group P6/m and cell constants $a = 15.05399(5)$ Å and $c = 3.96845(2)$ Å. Some of the important structural details for the new compound are given in Table 4.2, and the preliminary crystal structure is shown in Figure 4.9.
Table 4.2 Preliminary structural data for the novel phase Na$_{0.7}$Ge$_{1}$, space group P6/m, $a = 15.05399(5)$ Å, $c = 3.96845(2)$ Å.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$X$</th>
<th>$y$</th>
<th>$Z$</th>
<th>$U_{iso}$ (Å$^2$)</th>
<th>Site Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge1</td>
<td>0.37332(8)</td>
<td>0.26958(8)</td>
<td>0</td>
<td>0.0115(4)</td>
<td>1</td>
</tr>
<tr>
<td>Ge2</td>
<td>0.04088(9)</td>
<td>0.59174(8)</td>
<td>0</td>
<td>0.0106(4)</td>
<td>1</td>
</tr>
<tr>
<td>Ge3</td>
<td>0.52012(9)</td>
<td>0.15164(9)</td>
<td>$\frac{1}{2}$</td>
<td>0.0052(3)</td>
<td>1</td>
</tr>
<tr>
<td>Ge4</td>
<td>0.48411(10)</td>
<td>0.30138(7)</td>
<td>$\frac{1}{2}$</td>
<td>0.0071(3)</td>
<td>1</td>
</tr>
<tr>
<td>Na5</td>
<td>$\frac{2}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>0</td>
<td>0.02</td>
<td>1</td>
</tr>
<tr>
<td>Na6</td>
<td>0.2539(6)</td>
<td>0.0639(7)</td>
<td>$\frac{1}{2}$</td>
<td>0.088(4)</td>
<td>0.617(9)</td>
</tr>
</tbody>
</table>

Figure 4.9 A schematic of the structure of NaGe$_{1}$, viewed along the $c$-axis at a slight tilt. Na atoms are shown in orange, the Ge atoms in dark pink. The hexagonal unit cell is enlarged in the upper right, with the crystallographic site designations labeled.
The material crystallizes in a complex zeolite-like structure, in which the framework of the structure is built from Ge while Na atoms are found to be situated inside the broad channel (Na6) as well as in the smaller hexagonal channels (Na5). In the broad channel, the six Na6 sites are related to each other by 6-fold symmetry. Note from Table 4.2 that while the Ge sites that define the framework of the structure are fully occupied, the Na sites in the broad channel (Na6) are only partially filled in the sample studied. If all sites are fully occupied, the chemical formula is NaGe₃. As a result of this partial occupancy, the chemical formula of this new phase is tentatively estimated to be Na₀·₇Ge₃, and the general chemical formula can be written as Na₁₋ₓGe₃. Also from Table 4.2, the Na atoms at the Na6 sites possess a relatively large isotropic displacement parameter, implying either a large static or dynamic disorder at these sites in the broad channel. In the center of the broad channel, residual electron density was observed at (0,0,½), the exact nature of which has yet to be determined.

Although the structural model proposed is preliminary, the model reproduces the experimental X-ray diffraction patterns very well. Figure 4.10 shows a simulated diffraction pattern calculated using the software PowderCell⁸⁸ for NaGe₃, i.e. with x = 0, as compared to an experimental X-ray diffraction pattern for Na₁₋ₓGe₃ collected at USF. As seen in the figure, the two patterns show excellent agreement in features, indicating the high quality of the preliminary model. The discovery of this new compound shows that there is still new science and complexity to be found in simple binary systems and its unique structure motivates further study which is currently underway by the author and coworkers.
Figure 4.10 Powder X-ray diffraction of Na$_{1-x}$Ge$_3$. The lower spectrum is a simulated XRD pattern for NaGe$_3$ ($x = 0$) calculated using the PowderCell program, with the Bragg reflections indexed. The upper spectrum is an experimental XRD pattern from a Na$_{1-x}$Ge$_3$ sample. The two patterns show very good agreement in peak positions and relative intensities.
Possibly the most interesting aspect of clathrate compounds is the transport phenomena these materials exhibit. The transport properties of several of the samples synthesized in this work have been studied. New transport phenomena in type II clathrates are presented, with a central result of this work being that the transport properties of type II clathrates depend strongly on the guest content and on framework substitution.

5.1 Experimental Details

All transport measurements were performed using a custom built apparatus, consisting of a closed-cycle helium cryostat (Janis), Keithley Instruments 2100 multimeter and 2400 current sourcemeters, and a Lakeshore temperature controller. Samples were mounted on a custom designed sample holder, allowing electrical resistivity, Seebeck coefficient, and thermal conductivity measurements to be performed on the same sample simultaneously during the same measurement cycle. Resistivity measurements were performed using a standard four-probe arrangement. Seebeck coefficient measurements were performed at each temperature by controlled sweeping
through temperature gradient and measurement of the corresponding voltage difference, the slope of the straight line fit yielding the Seebeck coefficient. For thermal conductivity, multiple temperature differences are stabilized at each temperature, and the slope of applied power versus temperature difference yields thermal conductance, from which thermal conductivity is extracted. For all three measurements, geometrical considerations determine the largest portion of uncertainty in the measurement. For resistivity and thermal conductivity, the largest source of uncertainty results from the measurement of the cross-sectional area and contact separations, the ratio of which is known as the geometrical factor. For Seebeck measurements, placement of the voltage and thermocouple contacts such that they lie in the same cross-sectional plane is crucial. The room temperature uncertainty in the transport measurements is estimated to be 3.5% for resistivity, 5% for Seebeck coefficient, and 10% for thermal conductivity. Details of the transport measurement system and sample mounting process can be found in Ref. 70.

5.2 Transport Properties of Na$_x$Si$_{136}$ Clathrates

As noted previously, the transport properties of Na$_x$Si$_{136}$ clathrates have not been well characterized, though these materials were some of the first inorganic clathrates to be synthesized almost forty years ago.$^{10}$ In the present work electrical resistivity and thermal conductivity measurements were performed on samples with compositions Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$. To the best of our knowledge, there exist no previous reports on the thermal conductivity of Na$_x$Si$_{136}$ clathrates.
Figure 5.1 Temperature dependent electrical resistivity of Na$_{1}$Si$_{136}$ (closed circles) and Na$_{8}$Si$_{136}$ (open circles), along with Cs$_{8}$Na$_{16}$Si$_{136}$ (closed squares).

Temperature dependent electrical resistivity measurements for Na$_{1}$Si$_{136}$, Na$_{8}$Si$_{136}$ and Cs$_{8}$Na$_{16}$Si$_{136}$ are shown in Figure 3. The data for Cs$_{8}$Na$_{16}$Si$_{136}$ are taken from Ref. 25. The lack of low temperature measurements for the Na$_{1}$Si$_{136}$ specimen below 150 K is due to the exceedingly high resistivity. The effect of the alkali is evident, with the room temperature values for the resistivity spanning seven orders of magnitude between Cs$_{8}$Na$_{16}$Si$_{136}$ and Na$_{1}$Si$_{136}$, and the resistivity decreasing with increased alkali content. The “completely filled” stoichiometric clathrate Cs$_{8}$Na$_{16}$Si$_{136}$, which has Cs atoms inside all of the hexakaidecahedra and Na atoms inside the smaller dodecahedra, exhibits metallic conduction$^{25}$, while Na$_{1}$Si$_{136}$ and Na$_{8}$Si$_{136}$ show activated temperature
dependences. We note that since the density of these two specimens is relatively low (~ 70% of the theoretical X-ray density), there may be a large contribution to the resistivity due to poor contact between the polycrystalline grains. Thus the magnitude of the intrinsic resistivity of the materials may be lower than that shown in Figure 5.1. Nevertheless the data indicates the Na concentration directly influences the electrical properties. The room temperature resistivities for Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$ differ by approximately two orders of magnitude, in agreement with the trend in room temperature electrical conductivity reported by Cros et al.$^{11}$ Obtaining high density is a challenge in silicon-based clathrates and we are currently investigating different avenues in order to address this issue.

The lattice thermal conductivity, $\kappa_g$, as a function of temperature for Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$ is shown in Fig. 5.2 along with that of single crystal diamond-structure silicon.$^{98}$ The data for the type II silicon clathrates have been adjusted for porosity.$^{99,100}$ Since the resistivities of Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$ are large, thermal conduction by electrons can be neglected, assuming a Wiedemann-Franz relation, thus the thermal conductivity for these type II silicon clathrates can be regarded as entirely due to the lattice. Na$_1$Si$_{136}$ shows a very low $\kappa_g$, much lower than that of diamond-structure silicon. A similar result was found previously for the guest-free clathrate Si$_{136}$.$^{66}$ First principles calculations$^{101}$ of the thermal conductivity for a "guest-free" clathrate (hypothetical type-I Ge$_{46}$) indicated a ten-fold decrease in lattice thermal conductivity compared with that of the diamond-structure semiconductor (Ge) due to scattering of heat-carrying acoustic phonons by zone-boundary modes "folded back" due to the increase in unit cell size.$^{100}$ It is
interesting to note that the $\kappa$ values we reported for Si$_{136}$ are lower than that of Na$_1$Si$_{136}$, for temperatures less than 300 K ($\kappa_g$ at ~ 300 K are similar within experimental error). Although the reason for this is not entirely understood, the intensive processing needed to produce a completely empty clathrate, which involves repeated washing with concentrated acids and heat treatment under vacuum, could cause lattice defects, thus resulting in further lowering of the thermal conductivity relative to Na$_x$Si$_{136}$ clathrates that have not undergone such processing. Nevertheless, evidently low $\kappa_g$ values are achieved in clathrate compounds with few or no atoms inside the polyhedra, due to the intrinsic vibrational properties of the framework and the enlarged unit cell.
Though similar to that of Na\(_{136}\) for \(T < 20\) K, \(\kappa_g\) above 20 K for Na\(_{136}\) shows a lower \(\kappa_g\) with a very different temperature dependence compared with that of Na\(_{136}\). The magnitude is very low, similar to that of polycrystalline type I clathrates.\(^23\) In the range 50 to 70 K there is a clear “dip” in \(\kappa_g\). This feature in the temperature dependence of thermal conductivity has in the past been attributed to the resonance scattering of phonons by localized atomic or molecular vibrations.\(^{102,103,104}\) Such a feature can be understood qualitatively in terms of the thermal occupation of phonons. The interaction of localized vibrations with the heat carrying phonons in a solid will be strongest when the phonon frequency closely matches the frequency of the localized vibration, allowing for a resonant transfer of energy and scattering of the former. When the temperature is such that a significant population of phonons with frequencies near the resonant frequency carries the heat, a marked reduction in the thermal conductivity will result, hence causing a dip-like feature. Indeed, in type I clathrates such as Sr\(_{8}\)Ga\(_{16}\)Ge\(_{30}\) and Eu\(_{8}\)Ga\(_{16}\)Ge\(_{30}\),\(^{23,106}\) dips in the thermal conductivity were attributed to resonance scattering of the heat-carrying acoustic phonons by the localized vibrations of the guest atoms inside their cages, as shown in Figure 5.3. The significant suppression and dip-like feature of the thermal conductivity indicate a similar effect may be occurring in Na\(_{8}\)Si\(_{136}\) where one-third of the polyhedra are occupied by Na. From previous measurements on Cs\(_{8}\)Na\(_{16}\)Si\(_{136}\) and other stoichiometric type II clathrates using single crystal XRD,\(^{25}\) the atomic displacement parameters (ADP) suggest that the “guest” atoms in the type II clathrates undergo large amplitude, localized vibrations. These results were corroborated by Raman scattering experiments.\(^{63}\) Furthermore, inelastic neutron scattering
Figure 5.3 Low temperature lattice thermal conductivity for single crystalline Sr$_8$Ga$_{16}$Ge$_{30}$ (circles) and Eu$_8$Ga$_{16}$Ge$_{30}$ (squares).$^{105}$ The dashed line is data for amorphous SiO$_2$, and the solid lines at fits to the experimental data, which account for resonant phonon scattering. Reprinted figure with permission from G.S. Nolas, T.J.R. Weakly, J.L. Cohn, and R. Sharma, Phys. Rev. B 61, 3845 (2000). Web: http://link.aps.org/abstract/PRB/v61/p3845.

measurements of the phonon density of states$^{106}$ as well as theoretical calculations$^{64}$ indicate a strong interaction exists between the localized vibrations of the guests and the host phonon modes in type II clathrates. Optical and ultrasound measurements on Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$ specimens, along with an investigation into Na$_x$Si$_{136}$ specimens with varying Na concentrations, are currently underway.

The thermal conductivity data presented here for Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$ indicate that these materials are low thermal conductivity crystalline solids. In addition, $\kappa_g$ data on Na$_8$Si$_{136}$ may indicate localized disorder produced by the Na within the Si polyhedra
resulting in a further reduction in $\kappa_g$, as compared with low Na content type II silicon clathrates. To the best of our knowledge this constitutes the first evidence from transport measurements that the guest atoms have a dramatic effect on the thermal transport in type II clathrates.

### 5.3 Transport Properties of Cs$_8$Na$_{16}$Cu$_y$Ge$_{136-y}$ Clathrates

The electrical resistivity, Seebeck coefficient, and thermal conductivity of Cs$_8$Na$_{16}$Cu$_y$Ge$_{136-y}$ clathrates with $y = 5$ and 8 are reported, and compared to Cs$_8$Na$_{16}$Ge$_{136}$ ($y = 0$). All data shown for Cs$_8$Na$_{16}$Ge$_{136}$ ($y = 0$) were taken from Ref. 25. It is shown that Cu substitution for Ge on the framework has a significant effect on all of the transport properties in these materials.

Figure 5.4 shows the temperature dependence of the resistivity for Cu substituted samples. The effect of substituting Cu is an increase in the magnitude of the resistivity with increasing Cu concentration. All three materials exhibit metallic behavior, with resistivities that increase approximately linearly with temperature. To our knowledge, no theoretical calculations exist for the electronic structure of framework-substituted type II clathrates, though calculations$^{32}$ for Cs$_8$Na$_{16}$Ge$_{136}$ indicate this material to be a metal with a Fermi level clearly within the conduction band, consistent with both transport$^{25}$ and NMR$^{61}$ measurements. In a simplified interpretation, the electropositive guests in clathrates can donate their valence electrons to the framework. The Cu in the framework would act as a “trivalent acceptor,” since three electrons are needed to become
isoelectronic with Ge and participate in the tetrahedral bonding. Thus we can write the expression \( (\text{Cs}^{1+})_8(\text{Na}^{1+})_{16}(\text{Cu}^{3-})_y\text{Ge}_{136-y} \). Within this picture, increasing the copper content would correspond to decreasing the number of majority carriers per formula unit. This simplified picture is consistent with our resistivity measurements. In addition, the increased impurity scattering of the charge carriers by the Cu ions on the framework is a likely contributor to the increase in magnitude of the resistivity with increasing Cu content.

Measurements of the Seebeck coefficient \( (S) \) for these materials yielded interesting results, as shown in Figure 5.5. As expected for materials possessing metallic properties, the magnitudes of the Seebeck coefficients for the three samples are all
relatively low. Upon Cu substitution from $y = 0$ to $y = 5$, the magnitude of the Seebeck coefficient increased by approximately a factor of 2 at 300 K. This is consistent with the increase in resistivity found for this Cu content, and the simple picture outlined above. However, perhaps the most interesting aspect of the data is for the Cu content of $y = 8$. This material shows a very small value of $S$ of $-1.6 \, \mu V/K$ at 300 K, which quickly decreases to zero at approximately 230 K, and then changes sign below this temperature. As the sign of the Seebeck coefficient is indicative of the type of majority charge carrier, the transition from negative to positive $S$ indicates a transition from electron (n-type) to hole (p-type) conduction. This result constitutes the first observation of p-type conduction in type II clathrates, and shows that framework-substitution in type II clathrates has a

![Figure 5.5](image_url)

**Figure 5.5** Temperature dependence of the Seebeck coefficient for Cs$_8$Na$_{16}$Cu$_y$Ge$_{136-y}$, with $y = 0, 5, 8$. The sample with $y = 8$ shows p-type conduction below 220 K.
significant effect on the electrical properties in these materials. Within the simplified picture given above, the composition $y = 8$ corresponds to exact compensation of the 24 electrons per formula unit “donated” by the alkali guests to the framework, and the low magnitude and change of sign of the Seebeck coefficient may indicate dual conduction in this material. Again, theoretical calculations of the electronic structure in these materials may help to elucidate the underlying physics.

The thermal conductivity was also found to be affected by the Cu substitution. Figure 5.6 shows the total measured and estimated lattice thermal conductivity. The thermal conductivity ($\kappa$) of a solid is typically expressed as the sum of electronic ($\kappa_e$) and lattice ($\kappa_g$) contributions, so that $\kappa = \kappa_e + \kappa_g$. Since the Cs$_8$Na$_{16}$Cu$_y$Ge$_{136-y}$ specimens behave as metallic conductors, there is expected to be a significant contribution from the

![Graph showing thermal conductivity](image)

**Figure 5.6** Thermal conductivity of Cs$_8$Na$_{16}$Cu$_y$Ge$_{136-y}$ with $y = 0, 5, 8$. (a) Total measured thermal conductivity. (b) Estimated lattice thermal conductivity.
charge carriers. To estimate the lattice thermal conductivity \( \kappa_g = \kappa - \kappa_e \) the electronic portion was estimated assuming the Weidemann-Franz relation \( \kappa_e = L_0 T / \rho \), where \( L_0 = 2.45 \times 10^{-8} \text{ V}^2/\text{K}^2 \) is the Lorenz number, \( T \) is the absolute temperature, and \( \rho \) is the measured electrical resistivity. This was then subtracted from measured thermal conductivity. In addition, as these samples were approximately 80\% of the theoretical X-ray density, the data were also corrected for porosity.\(^{99,100}\) The results are shown in Figure 5.6(b), and indicated a slight decrease in the magnitude of the thermal conductivity with increasing Cu content. The reduction could conceivably be due to point-defect scattering of phonons resulting from the difference in mass between Cu and Ge. No conclusive evidence was found here for resonance contributions to phonon scattering from the Cs or Na guests, though in the range 60 to 100 K, the same range in which the dip was observed for Na\(_8\)Si\(_{136}\), the thermal conductivity appears temperature independent for our \( y = 8 \) specimen.

The data all show a significant upswing in the thermal conductivity at the higher temperatures. A common source of error in thermal conductivity measurements is from radiation absorbed or emitted from the sample if it is not at the same temperature as its surroundings, since this is a source of power not accounted for in the measurement. This can be explained using the Stefan-Boltzmann law,

\[
P = \varepsilon A \sigma (T_0^4 - T_S^4) = C (T_0^4 - T_S^4),
\]

where \( P \) is the total power radiated or absorbed, \( \varepsilon \) is the emissivity of the sample, \( \sigma \) is the
Stefan-Boltzmann constant, $A$ is the surface area of the sample, $T_0$ is the temperature of the sample, $T_S$ is the temperature of the surroundings, and $C = \varepsilon A \sigma$ is a constant. During measurement of the thermal conductivity, the sample is not at uniform temperature, since a temperature difference of order $\Delta T \sim 0.5 \text{ K}$ is applied to the sample. If we assume the surroundings are at $T_S = T$, and the sample is at $T_0 = T + \Delta T$, we have

$$P = C \{(T + \Delta T)^4 - T^4\}$$
$$= C \{T^3 \Delta T + O((\Delta T)^2)\}$$
$$\approx C T^3 \Delta T. \quad (5.2)$$

We have ignored terms of order $(\Delta T)^2$ and higher, since at all temperatures of interest $T >> \Delta T$. It is clear then that this radiation effect should follow a $T^3$ temperature dependence, and should be more important at higher temperatures. Figure 5.7 shows a method by which the presence of effects from radiation can be verified, using the Cs$_8$Na$_{16}$Ge$_{136}$ sample as an example. The thermal conductivity is extrapolated from the mid-range temperature dependence, as indicated by the dashed line. This extrapolated portion is then subtracted from the measured portion, giving the difference $\Delta \kappa$. If there are significant radiation losses present, this difference is expected to follow a $T^3$ dependence, as described above. As shown in the inset, this was found to be the case indicating that the upswing is in fact likely due to radiation losses from the sample. Similar analysis was performed for the two Cu substituted samples, which also showed similar results. We note that the effect was much smaller in the Cu samples (see Figure 5.6), as compared to the Cs$_8$Na$_{16}$Ge$_{136}$ sample which was measured on a system
Figure 5.7 Verification of losses due to radiation during the thermal conductivity measurement. The dashed line represents the thermal conductivity extrapolated from the mid-range temperatures. The inset shows the $T^3$ dependence of $\Delta\kappa$, indicating the upswing at the higher temperatures is likely due to radiation losses from the sample.

elsewhere,$^{25}$ indicating that the losses due to radiation are small for our measurement system in the Novel Materials Laboratory, reinforcing the high quality of our transport measurements system.
Summary and Future Directions

The impetus for the present work throughout has been the need for deeper experimental investigation into the synthesis and physical properties of type II clathrates. This follows from the unique and interesting properties these materials possess, their potential for technological applications, and the significantly less attention that type II clathrates have received thus far as compared to the type I structural subset. In particular, a better understanding of the possible composition space for type II clathrates is needed in order to better quantify the prospects these materials hold for applications. In this section, some of the key results of this work are reviewed, and directions for future work are discussed.

The present work has utilized a range of synthesis and characterization techniques to explore new type II clathrate compositions, as well as to study the structural and transport properties of these materials. For the first time, it has been shown that type II clathrates are stable under substitution of the framework species. The substitution of Cu for Ge in $\text{Cs}_8\text{Na}_{16}\text{Cu}_y\text{Ge}_{136-y}$ type II clathrates is found to significantly affect the transport properties, in particular the electronic transport. For Cu content of $y = 8$, a transition from n-type to p-type majority conduction is observed below room temperature, the first such
observation of hole conduction in type II clathrates to date. These initial results suggest the possibility that the electrical properties of type II clathrates could be controlled via appropriate framework substitution, and give new direction for expanding the possible compositions in type II clathrates.

An extensive investigation has been undertaken into the synthesis of type II clathrates by route of degassing of alkali and alkaline earth silicides and germanides. Na$_{x}$Si$_{136}$ clathrates, materials whose wide optical band gap is raising interest for photovoltaic applications, have been successfully synthesized covering a range of Na content, with significantly less type I Na$_8$Si$_{46}$ clathrate present as impurity as compared to the research found in the literature. Na$_x$Si$_{136}$ samples with $x = 1, 8$ have been studied in greater detail. These materials are stable up to 600$^\circ$C, an encouraging result for higher temperature applications. The electrical transport in these materials show resistivities that decrease with Na content, and activated temperature dependences for Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$. This compared with the metallic behavior of the “fully loaded” Cs$_8$Na$_{16}$Si$_{136}$ shows that the properties of type II silicon clathrates depend strongly on the guest atom content and/or type. Indeed, the thermal conductivity measurements on theses materials also revealed striking results. Na$_1$Si$_{136}$ and Na$_8$Si$_{136}$ clathrates are shown to be low-thermal conductivity crystalline materials, in agreement with previous work on the completely unfilled clathrate Si$_{136}$. Although these compounds appear to be “intrinsically” poor conductors of heat, the introduction of guest Na atoms into the cages in Na$_8$Si$_{136}$ have a further dramatic effect. The thermal conductivity is reduced even lower, and the data show an unmistakable dip in the temperature dependence. As this
phenomena has in the past been associated with resonant phonon scattering phenomena, this may constitute the first evidence that localized vibrations of the guests in type II clathrates may scatter the heat carrying phonons in type II clathrates, as has also been found in type I clathrates. This warrants further investigation into the dynamics of the guests, which is currently underway.

One challenge in the silicon-based type II clathrates is achieving high density in the compacted polycrystalline samples. Currently used hot-pressing techniques have produced samples with densities of the order of 70% of the theoretical X-ray density. Although the clathrate framework was found to be stable to relatively high temperatures, hot-pressing at elevated temperature is excluded as a possibility due to the sensitivity of the composition $x$ with temperature. This combined with the rigidity of the silicon framework, and the inherent oxide layer that is ubiquitous in silicon materials, presents obstacles to obtaining high density in Na$_x$Si$_{136}$ clathrates. One possible route being investigated is Spark Plasma Sintering (SPS). In this method, high current densities are passed through a sample, resulting in internal Joule heating, as opposed to external heating of the press die with a heater coil as in conventional hot-pressing techniques. This may hold promise in ensuring good contact between the grains through breaking of the oxide layer, with the added advantage of densification at lower temperatures.

A number of other silicides and germanides were also investigated. Analysis of the synthesis results, as well as the published literature revealed relationships between the crystal structures of the intermediate compounds and synthesis products observed. A systematic investigation into the synthesis of Na$_x$Ge$_{136}$ did produce the clathrate, however
the yield was too small and of poor quality to produce samples for transport measurements. Rather the dominant phase over a range of several tens of degrees Celsius consisted of a newly discovered compound of general chemical formula Na$_{1-x}$Ge$_3$. The structural solution of the material revealed a novel crystal structure, and this new material warrants further study which is currently underway.

In summary, this work has expanded the currently small body of knowledge that exists concerning type II clathrate materials, as well as opening new doors in the synthesis of clathrates. These materials continue to attract interest due to the unique properties they possess, and the prospects they hold for useful applications. This work has shown clearly that type II clathrates offer a class of materials in which new physics, materials science, and solid state chemistry can be discovered.
References

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Bibliography