

Project Title: A Fundamental Study of Inorganic Clathrate and Other Open-Framework Materials

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Summary

Clathrates are “open-structured” materials with a host framework that has the ability to encage guest atoms or molecules. There are many interesting physical properties observed in clathrates, including glass-like thermal conductivity, superconductivity in *sp*³ bonded solids, magnetism, and heavy atom tunneling in the crystalline state.[1] These physical properties are a direct consequence of their structural properties and make clathrates promising for a range of useful applications, from thermoelectrics to photovoltaics, as well as potentially ultra-hard materials. The key findings from this project that are described in detail below, in the Project Results and Discussion section, include:

- Optimized synthesis and structural properties of microcrystalline Na_xSi₁₃₆ clathrates.
- Synthesis of a new “open framework” phase, Na_{1-x}Ge_{3+z}, employing our synthetic approach.
- Crystal growth and transport properties measurements on single-crystal clathrates, for the first time, by employing Spark Plasma Sintering.
- Selective clathrate crystal growth by employing a process whereby reaction of the vapor phase with spatially separated graphite, in a closed volume, allows for control of Na vapor pressure: Kinetically Control Thermal Decomposition (KCTD).
- Used these techniques to synthesize and structurally characterize Na_xSi₁₃₆ ($0 < x < 24$) single crystals for the first time.
- Measured the temperature-dependent transport properties of Na_xSi₁₃₆.
- Grew and characterized single crystals of K₈Si₄₆ and K₁₇Si₁₃₆.
- Selective synthesis of clathrates employing SPS by tuning the SPS parameters.
- Investigated the pressure effects on crystal size for SPS crystal growth.
- Si-Ge clathrate alloys synthesized for the first time by SPS and KCTD.
- Began an investigation into ionic liquid synthesis of clathrate compositions.
- Single crystal and microcrystalline Na₈Al₈Si₃₈ synthesized, for the first time, by KCTD and SPS by employing multiple precursors allowing for structure and transport properties investigations of Na₈Al₈Si₃₈.
- Simultaneous electrochemical redox and ion-exchange reactions: A new approach for inorganic clathrate synthesis and crystal growth.
- Quaternary clathrate-II Cs₈Na₁₆Al₂₄Si₁₁₂ synthesized by multi-precursor, ion-exchange reaction employing KCTD, and its low temperature transport properties measured, for the first time.
- Clathrate-II (K,Ba)₁₆(Ga,Sn)₁₃₆ compositions synthesized and densified into dense polycrystalline form employing SPS; structure and transport properties investigated.
- Type-II clathrate with a Li-Ge framework synthesized and characterized.
- Densified nanocrystals into dense polycrystalline solids with nano-scale grains via SPS for transport properties investigations.

Background

Due to formidable synthetic challenges, many materials of scientific and technological interest are first obtained as microcrystalline powders. High purity, high yield processing techniques are often lacking and thus care must be taken in interpretation of the observed structural, chemical, and physical properties of powder or polycrystalline materials, which can be strongly influenced by extrinsic properties. Furthermore, the preparation of high-quality single crystals for many materials by traditional techniques can be especially challenging in cases where the elemental constituents have greatly differing melting points and/or vapor pressures, when the desired compound is thermodynamically metastable, or where growth with participation of the melt is generally not possible. New processing techniques are therefore imperative in order to investigate the intrinsic properties of these materials and elucidate their fundamental physical properties.

Intermetallic clathrates constitute one such class of materials. The complex crystal structures of intermetallic clathrates are characterized by mainly group 14 host frameworks encapsulating guest ions in polyhedral cages. The unique features of clathrate structures are intimately related to their physical properties, offering ideal systems for the study of structure-property relationships in crystalline solids. Moreover, intermetallic clathrates are being actively investigated due to their potential for application in thermoelectrics, photovoltaics and opto-electronics, superconductivity, and magnetocaloric technologies.

We have developed different processing techniques in order to synthesize phase-pure high yield clathrates reproducibly, as well as grow single crystals for the first time. We also employed these techniques to synthesize new “open-framework” compounds. These advances in materials processing and crystal growth allowed for the investigation of the physical properties of a variety of different clathrate compositions for the first time.

Introduction

Clathrates, or “open-framework” complexes are sometimes thought of as inclusion compounds. Several families of clathrates are known, the host lattices can be organic or inorganic. The most important and well-studied of these possess similar structure types as that of the clathrate hydrates,[1] where face-sharing polyhedra enclose guest species. Clathrate hydrates have been known for two centuries, whereas isostructural inorganic compounds, in which Si, Ge and Sn elements form the host lattice and alkali-metals, alkaline-earth or less-common metals are the guest species, have been more recently investigated. In all cases, tetrahedral bonding forms the framework, with guest species occupying the relatively large “voids” inside the polyhedral “cages”.

A large majority of the characteristic polyhedral cages that form the framework of clathrate structures exhibit twelve pentagonal faces typically in combination with a lower number of polyhedra that contain hexagonal faces, according to Euler’s rule for polyhedrons. The smallest and most frequent of these is the pentagonal dodecahedron, with only 12 pentagonal faces, 20 vertices and 30 edges, more simply referred to as 5^{12} , and continue in increasing size: $(5^{12}6^2)$, 3 $(5^{12}6^3)$, 4 $(5^{12}6^4)$ and 8 $(5^{12}6^8)$ hexagonal faces. Most of the known clathrate structure types are composed of a combination of two of these polyhedra that form large and highly symmetrical unit cells involving, for example, 46 or 136 atoms in the framework lattice for the clathrate-I and

clathrate-II structure types, respectively. Whatever the arrangement of these polyhedral cages, the host species are tetrahedrally bonded with similar bond angles, close to 108° pentagonal angles and 120° hexagonal angles. Clathrate host lattices can therefore be considered as open forms of tetrahedrally bonded structures. It should therefore come as no surprise that that clathrate analogues, clathrasils, also exist with silica as the host lattice as this is another well-known tetrahedrally bonded structure. In addition, most clathrate structures have a simple relationship with those of well-known metal alloys, such as the Cr_3Si and MgCu_2 , in which the metal atoms are located on the same positions as the guest species inside the framework polyhedra would be, or where voids exist. Such alloys can therefore be thought of as templates for clathrate structures.

Another very interesting feature of clathrates is that the characteristic polyhedra, made of edge-sharing pentagonal and hexagonal faces, are related to the fullerene forms of carbon, the structures of which are based on the same geometrical rules. The C_{60} buckyball is formed by 12 pentagonal faces sharing edges with 20 hexagonal faces ($5^{12}6^{20}$). Clathrate polyhedra can be thought of as corresponding to the smallest possible fullerene clusters and form 3-D frameworks in order to neutralize the strains due to dangling bonds, whereas all the valence electrons are engaged in single or double bonds in a C_{60} buckyball enabling it to form isolated clusters. Due to their special cage-like architecture, and the relations they have with hydrates, clathrasils, inter-metallic alloys and fullerenes, the structures of inorganic clathrates are truly unique.

The inorganic clathrates $\text{Na}_8\text{Si}_{46}$ and $\text{Na}_x\text{Si}_{136}$ ($3 \leq x \leq 11$) were discovered five decades ago, and their structures identified by comparison with those of the clathrate hydrates.[1, 2] Over the past two decades research on inorganic clathrates has intensified due to their unique structure-property relationships as well as their potential for energy-related applications, including thermoelectrics and photovoltaics.[1] Within this time period standard synthetic approaches were employed in the preparation of compositions for investigation; however, it soon became clear that many compositions of interest were unattainable by traditional synthetic techniques.

Due to the efforts from several different research groups, and specifically the research under this project, substantial research has been undertaken resulting in a great deal of knowledge on these unique materials. Fundamental structure-property relationships have been revealed. In addition, certain compositions and structure types show promise for technological applications. Inorganic clathrate research is therefore a field of research that continues to be of interest to the scientific community. Given the current level of understanding in the field, there is no doubt that the research under this project resulted in extensive advances, if not the most important advances, in research on inorganic clathrates and an understanding of their transport properties.

Project Results and Discussion

High yield synthesis of microcrystalline clathrates

We prepared $\text{Na}_x\text{Si}_{136}$ clathrates via an optimized variant of the thermal decomposition (“flash degassing”) technique of the Zintl compound Na_4Si_4 under vacuum in order that the physical properties of $\text{Na}_x\text{Si}_{136}$ clathrates be thoroughly characterized for the first time.[3] This approach was reproducible and resulted in high yield processing of microcrystalline specimens. We achieved this with a custom-designed furnace system that allowed for the synthesis of $\text{Na}_{24}\text{Si}_{136}$ in relatively large quantities without decomposition of the type II clathrate phase. Figure 1 illustrates the clathrate-II crystal structure. The Na content is then varied by further heating under vacuum at temperatures between 360 and 425°C, the temperature and duration of heating determining the final Na content. The synthesis was scaled to produce over one gram of high quality $\text{Na}_x\text{Si}_{136}$ (a ten-fold increase over previous results)[3] in a single synthesis run, resulting in enough material to begin a detailed structural analysis of these materials. This work revealed insight into the structural response of the lattice to Na filling for $\text{Na}_x\text{Si}_{136}$ the first time. As shown in Figure 2, at higher Na content ($x > 8$) increased filling results in an expansion of the structure; however, at lower Na content ($x < 8$) the lattice parameter decreases with increasing Na content. The results are linked to the relative occupation of the two distinct cages in the structure, as determined from Rietveld structural refinement results.[3] At lower Na contents ($x < 8$) only the larger Si_{28} cage (8b site) is occupied, with the Si_{20} (16c) sites being completely empty. The latter sites only begin to be occupied once the Si_{28} cages are full. This indicates that Na preferentially occupies the Si_{20} cages for $x < 24$. Thus filling of the smaller Si_{20} cages (for $x > 8$) results in an expansion of the structure, while filling of only the larger Si_{28} cages ($x < 8$) results in a slight but clear shrinking of the structure. This is the first unequivocal experimental evidence of this effect in group 14 clathrate-II materials, and is due to particular electrostatic interactions between guest and cage as well as charge transfer from guest to framework. This result indicates the compositions thus far investigated contain Na inside the Si_{28} hexakaidecahedra and further corroborates the dynamic disorder, or “rattling”, nature of Na inside the large hexakaidecahedra formed by Si. This structural analysis plays an important role in correlation with the physical properties of these $\text{Na}_x\text{Si}_{136}$ in the complete Na range of compositions ($0 < x < 24$), as will be described below.

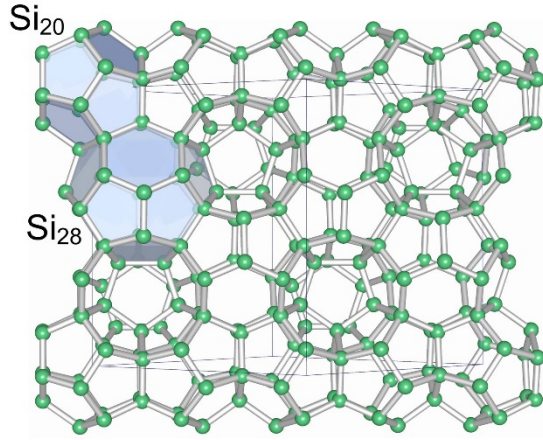


Figure 1. The cubic (space group $Fd\bar{3}m$) silicon clathrate-II framework, $\text{Si}(cF136)$. The two silicon cages that can be occupied by Na are highlighted in the upper left.

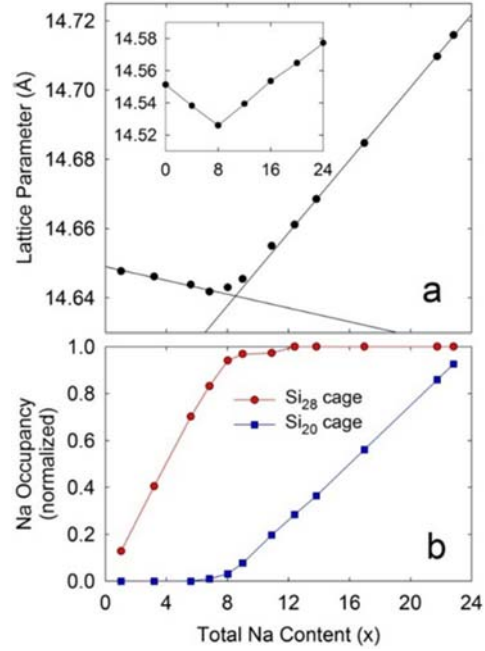


Figure 2. (a) Experimental normalized cage occupancies for Na@Si_{20} and Na@Si_{28} and (b) experimental cubic unit cell parameters, both as a function of total Na content. Inset (same units as main figure): Theoretical lattice parameters obtained from density functional theory calculations.

Ternary and quaternary clathrates, including framework substitution, were synthesized and characterized. We demonstrated that transition metals such as Ag [4] and Cu [5] can be substituted for Ge on the framework of ternary clathrate-II compounds such as $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$. Our single crystal X-ray diffraction studies [4] of $\text{Cs}_8\text{Na}_{16}\text{Ag}_y\text{Ge}_{136-y}$ revealed that this substitution preferentially occurs at the 96g framework site. This is likely linked to the local symmetry of this site, supporting the most “distorted” bonding geometry in the framework, as this has the highest number of unequal bond angles, and also the largest deviation ($\sim 120^\circ$) from the “ideal” tetrahedral bond angle of 109.5° . [4] In addition, our work on Cu substitution for Ge in $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$ was shown to influence the transport properties of this material (Figure 3). [5] We note these Ge-based materials are readily densified employing standard techniques such as hot pressing, unlike $\text{Na}_x\text{Si}_{136}$. [3] The electrical transport of $\text{Cs}_8\text{Na}_{16}\text{Cu}_y\text{Ge}_{136-y}$ clathrates is indicative of behavior typical of a metallic or heavily doped semiconductor material. This can be qualitatively understood in terms of a simplified “rigid band” model, in which the alkali guests (Cs and Na) donate electrons to the Ge and Ge-Cu framework conduction bands resulting in a relatively high concentration of carriers. [6] Hall measurements indicate electrons to be the majority carriers. The four-coordinated covalent bonding in the Ge_{136} framework is analogous to the sp^3 bonding found in elemental diamond structure Ge, in which substitutional Cu has been shown to behave as an electronic acceptor. [7] Our data are consistent with that found in the diamond structured analogue, indicating

partial charge compensation as a result of Cu substitution on the Ge framework.[5] The thermal conductivities of the two specimens show very similar temperature dependences, as expected since a considerable electronic contribution to the thermal conductivity is expected. We note that semiconducting filled type II clathrates are in general expected to possess relatively low lattice thermal conductivity, κ_L , due to their enlarged unit cell and potential phonon scattering as a result of large amplitude anharmonic guest atom vibrations.[1, 4, 6, 8]

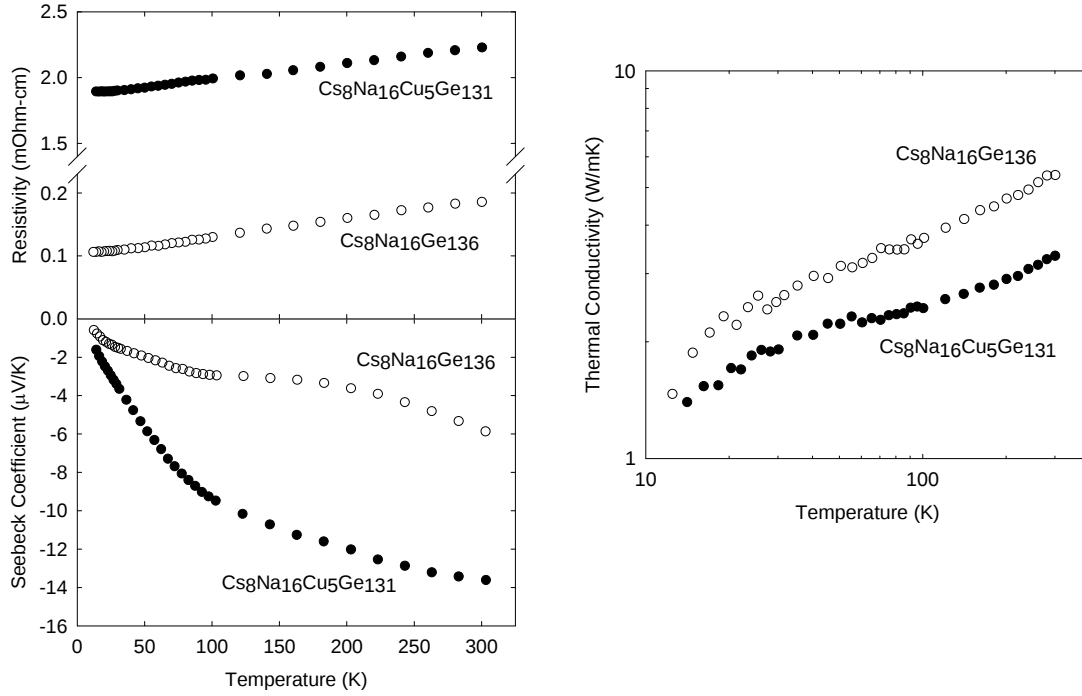


Figure 3. Temperature dependence of the electrical resistivity and Seebeck coefficient (left) and thermal conductivity (right) for $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$ (open symbols) and $\text{Cs}_8\text{Na}_{16}\text{Cu}_5\text{Ge}_{131}$ (filled symbols).

The discovery of a new binary framework phase, $\text{Na}_{1-x}\text{Ge}_{3+z}$, prepared by the new thermal decomposition of the binary Zintl phase Na_4Ge_4 was also achieved.[9, 10] The crystal structure is illustrated in Figure 4, and represents a new crystalline binary phase in the Na–Ge material system that had not previously been synthesized nor its crystal structure determined.[9] The hexagonal structure contains a covalently bonded framework of Ge atoms that form channels along the c -direction that encapsulate Na, akin to the channels found in some oxide zeolites. Transport measurements showed relatively large room temperature resistivity (of the order of 1 Ohm-m) and thermopower ($-380 \mu\text{V/K}$) with a very low thermal conductivity ($< 0.7\text{W/mK}$ at and below room temperature). This phase was very recently reproduced, and the structural features verified, by a high pressure synthesis approach in collaboration with the Carnegie Institute of Science.[11]

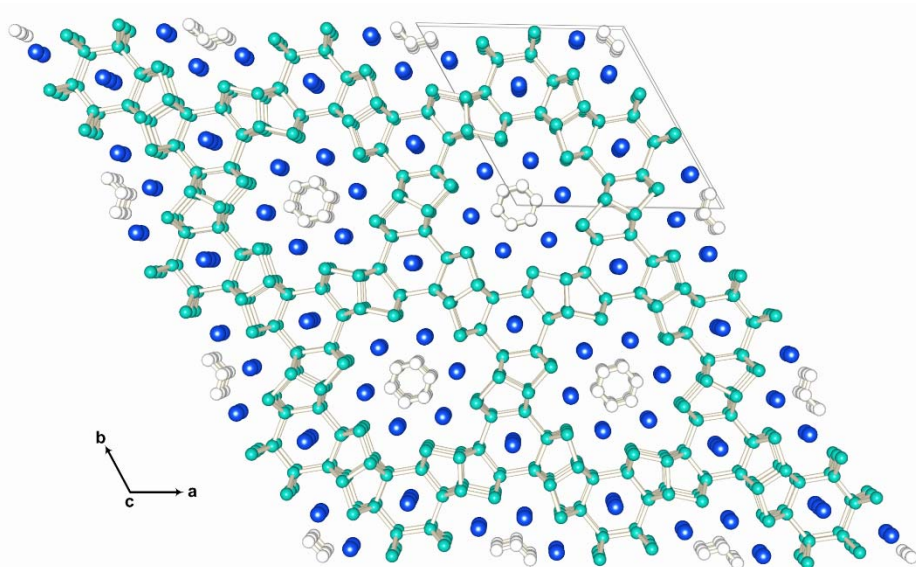


Figure 4. Crystal structure of the new zeolite-like framework phase, $\text{Na}_{1-x}\text{Ge}_{3+z}$, viewed down the c -axis. Na are represented by the blue circles and Ge by green and open circles. The six Ge atoms at the center of the channels represent six equivalent positions where one Ge atom may reside.

Clathrate crystal growth via Spark Plasma Sintering

The spark plasma sintering (SPS) technique, a variant of field-assisted processing, has in little more than a decade become an established consolidation method for fabrication of dense polycrystalline specimens. Pulsed DC electrical current is sourced through the specimen and die from the bottom electrode to the top electrode, which simultaneously act as the means for application of uniaxial pressure to the powder specimen. We demonstrated the effective use of SPS processing, as illustrated in Figure 5, for crystal growth of the intermetallic clathrate-II $\text{Na}_{24}\text{Si}_{136}$, [12] for which no route for single crystal preparation had been previously identified. $\text{Na}_{24-x}\text{Si}_{136}$ was the first intermetallic clathrate reported more than four decades ago, [2] however, until this work no method for single crystal growth of this material had been identified. [1] The process is driven by the electric field that is present during the SPS process and the formation and evaporation of Na formed at the cathode. We propose that $\text{Na}_{24}\text{Si}_{136}$ forms by oxidation of Si^{4+} at the anode (bottom electrode), whereas sodium is reduced at the cathode (top electrode). Upon oxidation of the Si^{4+} cluster anions in Na_4Si_4 , the clathrate framework is formed, while simultaneously encapsulating sodium in the resulting Si_{20} and Si_{28} cavities of the silicon framework. The yield of $\text{Na}_{24}\text{Si}_{136}$ crystals in the bottom portion of the compact increase as the reaction is allowed to progress for longer durations of time (Figures 6b and 6a). The observations shown in Figure 6 clearly suggest an influence of the DC electrical current. We propose that $\text{Na}_{24}\text{Si}_{136}$ forms by oxidation of Si^{4+} at the anode (bottom electrode), whereas sodium is reduced at the cathode (top electrode).

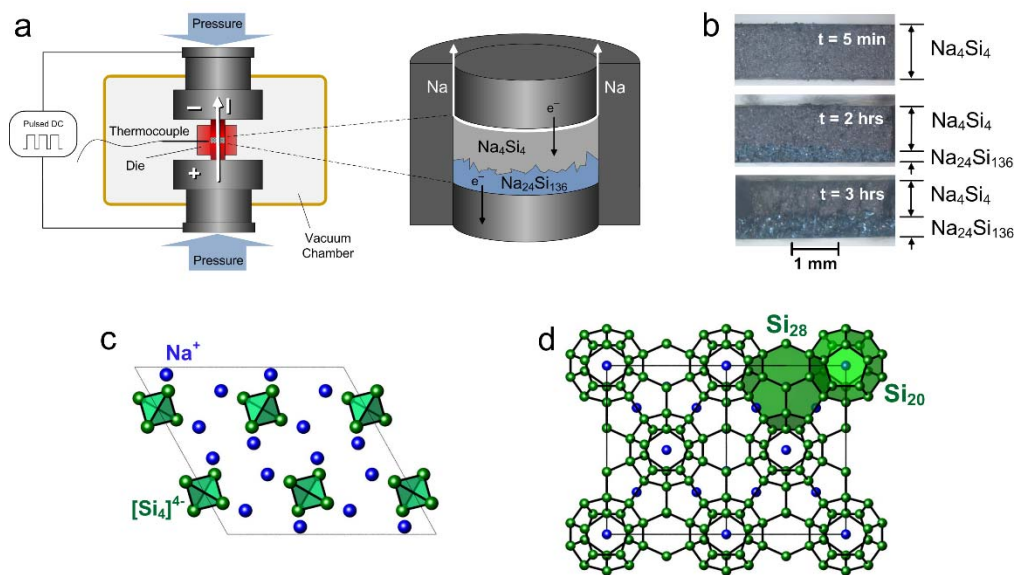


Figure 5 (a) Schematic of the spark plasma sintering (SPS) setup used for $\text{Na}_{24}\text{Si}_{136}$ crystal growth, with polarity of the applied voltage indicated. (b) Cross-sections of SPS-treated specimens, reacted at 600 °C and 100 MPa for 5 minutes, 2 hours, and 3 hours, as indicated. The upper portion consists of Na_4Si_4 while the lower, bluish crystalline fraction is clathrate-II $\text{Na}_{24}\text{Si}_{136}$. (c) Crystal structure of the Na_4Si_4 precursor. (d) Crystal structure of the clathrate-II $\text{Na}_{24}\text{Si}_{136}$. Oxidation of Na_4Si_4 promotes formation of the $\text{Na}_{24}\text{Si}_{136}$ clathrate, and the Si_{20} and Si_{28} coordination polyhedrons of the clathrate are highlighted.

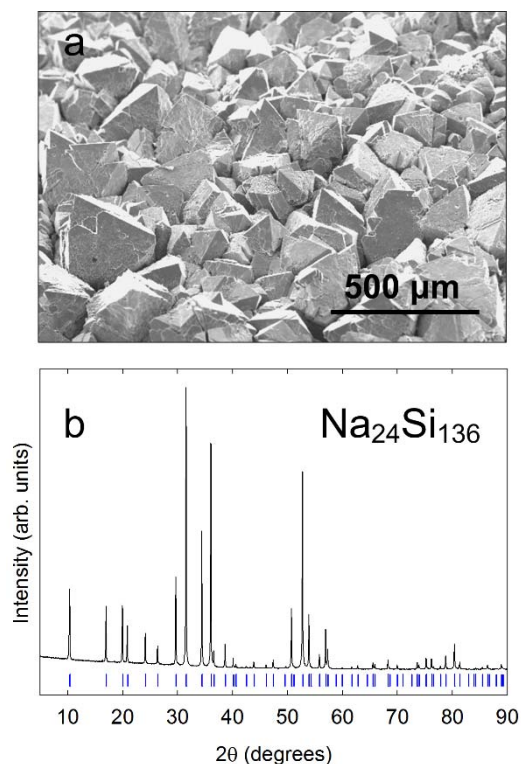


Figure 6 (a) Scanning electron microscope (SEM) secondary electron image of $\text{Na}_{24}\text{Si}_{136}$ crystals, after removal of residual Na_4Si_4 precursor by hydrolysis and dissolution. (b) Powder X-ray diffraction pattern for $\text{Na}_{24}\text{Si}_{136}$ grown at 600 °C after removal of residual Na_4Si_4 . All reflections correspond to $\text{Na}_{24}\text{Si}_{136}$, as illustrated by blue tick marks representing calculated reflection positions.

The PXRD pattern for a specimen ground from the $\text{Na}_{24}\text{Si}_{136}$ product is shown in Figure 6b, corroborating the phase purity of the specimen. All reflections are indexed with the clathrate-II crystal structure (space group $Fd\bar{3}m$, blue tick marks). The demonstrated synthesis of $\text{Na}_{24}\text{Si}_{136}$ by SPS thus constitutes a solution to a long standing challenge in the preparation of $\text{Na}_x\text{Si}_{136}$ clathrates: the previously known $\text{Na}_x\text{Si}_{136}$ synthetic routes, such as thermal decomposition or chemical oxidation of Na_4Si_4 , always produce the $\text{Na}_8\text{Si}_{46}$ clathrate in significant amounts.[13-15] This secondary phase is very difficult to avoid in the products from these synthetic routes. α -Si is also a common impurity phase in such specimens.[13-15] Several runs demonstrated that $\text{Na}_{24}\text{Si}_{136}$ is reproducibly prepared by SPS as single phase specimens.

The electronic structure of the silicon clathrate-II compositions have received considerable theoretical attention [16-19] in an effort to understand the influence of Na loading of the framework polyhedral cages on the electronic properties of this system. Electrical properties have been inferred from measurements on microcrystalline specimens,[20-21] but achieving a fundamental understanding of the conduction in these materials, and their physical properties more generally, has until now remained elusive.[22] Our preparation of $\text{Na}_{24}\text{Si}_{136}$ single crystals has allowed for structural and physical properties investigations on single crystal $\text{Na}_{24}\text{Si}_{136}$ clathrates for the first time.[23] Heat capacity was measured on single crystal specimens, and temperature dependent four-probe electrical resistivity, Seebeck coefficient, and steady-state thermal conductivity measurements were carried out by our custom designed and built closed-cycle helium cryostat [24]. The transport data were reproduced on several crystals. The temperature dependence showed excellent repeatability, and the magnitude agreed within the estimated relative uncertainty of associated with the determination of the geometrical factor for the crystals.

Single-crystal X-ray diffraction studies indicated an exceptionally large atomic displacement parameter (U_{eq}) obtained for Na ($8b$ site) in the Si_{28} cage (denoted hereafter as $\text{Na}@\text{Si}_{28}$) is suggestive of large amplitude thermal motion, or ‘rattling,’ for this Na guest within its oversized Si_{28} cage. Assuming a harmonic oscillator model (representing an Einstein mode associated with the Na guest), an estimate of the vibrational frequency, ν , can be obtained [25] from the room temperature $U_{\text{eq}} = 0.110(2) \text{ \AA}^2$, and the relation $U_{\text{eq}} = k_{\text{B}}T/[m(2\pi\nu)^2]$. Here k_{B} is Boltzmann’s constant, m is the mass of the Na atom, and $T = 293 \text{ K}$. Applying this model, a characteristic Einstein temperature $\Theta_{\text{E}} = h\nu/k_{\text{B}}$, where h is Planck’s constant, of 75 K is inferred using U_{eq} for $\text{Na}@\text{Si}_{28}$ when centered at the $8b$ site. Though this value of Θ_{E} is interpreted only as an estimate, it evidences the presence of a low-frequency phonon mode associated with the $\text{Na}@\text{Si}_{28}$ guest. Vibrational modes are more conclusively observed from the measured specific heat, where the presence of these entropic degrees of freedom is apparent.

The measured specific heat $C_p(T)$ for $\text{Na}_{24}\text{Si}_{136}$ is shown in Figure 7. Plotting the data as C_p/T^3 vs. T reveals clear evidence of low energy Einstein mode contributions to the specific heat. The data (Figure 7) reveals clear evidence of low energy Einstein mode contributions to C_p , which appear as a peak in the temperature dependence in this representation.[26] Considering the contributions to C_p that are expected to be significant in this temperature range [27], a model comprised of a linear combination of terms was fit to $C_p = C_e + C_{\text{E1}} + C_{\text{E2}} + C_{\text{D}}$ where $C_e = \gamma T$ is the electronic heat capacity, γ is the Sommerfeld coefficient,

$$C_{Ei}(T) = 3N_{Ei}R\left(\frac{\Theta_{Ei}}{T}\right)^2 \frac{\exp(\Theta_{Ei}/T)}{(\exp(\Theta_{Ei}/T)-1)^2} \quad \text{and} \quad C_D(T) = 9N_D R \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

Here N_{Ei} and Θ_{Ei} are the number (per formula unit) and Einstein temperature of oscillator i , respectively, and Θ_D is the apparent Debye temperature. The key aspect to note from this analysis, although several illuminating aspects were revealed,[23] is the analyses confirm the presence of a low energy Einstein-like mode (≈ 55 K) clearly associated with the eight Na@Si₂₈ guests per formula unit. This Θ_{E1} determined from C_p data is lower than that obtained from U_{eq} above, possibly corroborating the additional dynamic disorder. Nevertheless the frequency of this ‘‘rattle’’ mode falls well inside the frequency range of the host Si₁₃₆ acoustic phonon branches predicted from density functional theory calculations [28] indicating the potential for a resonant phonon interaction, analogous to clathrate-I materials.[29, 30] The value $\gamma = 0.163(4)$ JK⁻²mol⁻¹, determined from linear fits below 4 K in Figure 7, reflects a considerable electronic contribution to the specific heat and a substantial electronic density of states at the Fermi level typical of a metallic compound. This agrees with density functional calculations [31] for Na₂₄Si₁₃₆ which predict the Fermi level to coincide with a prominent peak in the electronic density of states, and also corroborates our metallic transport properties measurements.[23]

Observation of intrinsic electronic transport in Na-Si clathrates has been previously obscured by extrinsic effects originating in the microcrystalline nature of the specimens.[20, 22] The temperature dependent electrical resistivity, $\rho(T)$, data (Figure 8a) reveal metallic conduction, with ρ for the crystal reaching the value 0.03 mΩ-cm at 300 K. The Seebeck coefficient, S , (Figure 8a) reaches the value -5 μV/K at room temperature, consistent with a high density of electrons as the majority carriers and further corroborating metallic conduction.

At the lowest temperature of our measurement, 12 K, $d\rho/dT > 0$ indicating the residual resistivity for the specimen has still not yet been reached. Although a value for the residual resistance ratio (RRR) incorporating data from lower temperatures will be larger, we calculate from our data a RRR of $\rho(300\text{ K})/\rho(12\text{ K}) = 14$. To our knowledge, this value is several times larger than the highest RRR values reported before our research to this point for known metallic clathrates (i.e. with $d\rho/dT$ positive definite), including both polycrystalline [32] and single crystal clathrate-I specimens [33]. The relatively high RRR value for the Na₂₄Si₁₃₆ specimen, taken together with the above inferred mobility, is further indication of both the high quality of the crystal and the pronounced metallic conduction.

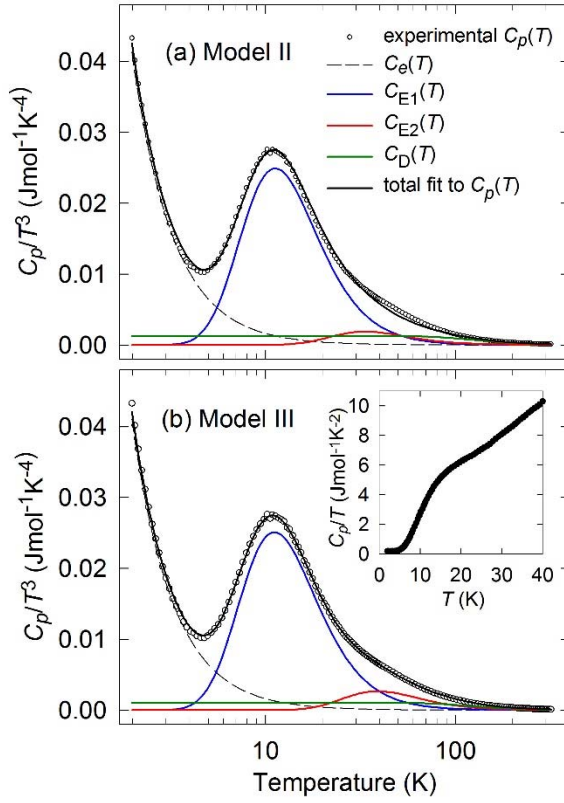


Figure 7 (a) Specific heat capacity of $\text{Na}_{24}\text{Si}_{136}$ plotted as C_p/T^3 against T , along with fits obtained with (a) Model II and (b) Model III described in Table I. Individual contributions to the overall fit are also shown as indicated. Inset to (b): The same experimental C_p data plotted as C_p/T against T , in the temperature range 0 to 40 K.

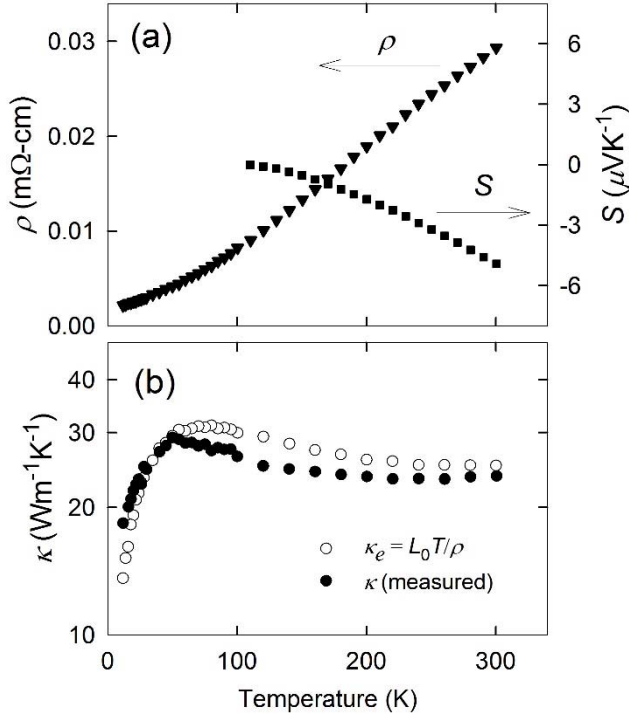


Figure 8 (a) Electrical resistivity (ρ) and Seebeck coefficient (S) of $\text{Na}_{24}\text{Si}_{136}$. (b) Thermal conductivity (κ) of $\text{Na}_{24}\text{Si}_{136}$ (closed symbols) and calculated contribution (open symbols) estimated from the Wiedemann-Franz relation.

The thermal conductivity, κ , of $\text{Na}_{24}\text{Si}_{136}$ (Figure 8b) is relatively large in comparison to other intermetallic clathrates. Indeed, the observed κ of $\text{Na}_{24}\text{Si}_{136}$ is substantially larger than previously observed for any intermetallic clathrate composition. Considering the pronounced metallic character observed in both C_p and ρ , a sizeable electronic contribution, κ_e , to the thermal conduction is expected. In a first approximation, employing the Wiedemann-Franz relation $\kappa_e = L_0 T / \rho$, with a temperature independent Lorentz number $L_0 = 2.45 \times 10^{-8} \text{ V}^2 \text{ s}^{-2}$ and the measured ρ , (Figure 8a) an estimate of κ_e is plotted in Figure 8b along with the experimentally measured thermal conductivity. Considering the low κ of the empty Si_{136} framework,[34] the presence of the low energy Einstein-like ‘rattle’ mode clearly observed in the measured specific heat and discussed above, and the considerable expected electron-phonon scattering in light of the high density of conduction electrons, it is reasonable to conclude that κ_L of $\text{Na}_{24}\text{Si}_{136}$ is very low in this composition compared to the large κ_e component.

Kinetically Controlled Thermal Decomposition (KCTD)

We have introduced and optimized a novel method for the selective synthesis of single-crystal clathrate-I $\text{Na}_8\text{Si}_{46}$ and clathrate-II $\text{Na}_{24}\text{Si}_{136}$ for the first time.[35] The alkali metal was slowly removed from the Na_4Si_4 precursor by reaction of the vapor phase with spatially separated graphite, in an effectively closed volume under uniaxial pressure. We named this new and unique process Kinetically Control Thermal Decomposition.[35] This resulted in the single-crystal structure refinement for $\text{Na}_8\text{Si}_{46}$ for the first time.[36] In both phases, full occupation of all Si framework sites was observed, and both cages in the two clathrate structures were found to be fully occupied by the Na guests confirming stoichiometric compositions. Substantial disorder (large isotropic atomic displacement parameters, U_{eq}) is observed for the guest Na inside Si_{28} in $\text{Na}_{24}\text{Si}_{136}$, in agreement with the “rattling” phonon mode and off-centering associated with this guest Na ion.

In our new KCTD processing technique, alkali metal is removed from the Na_4Si_4 precursor by reaction of the vapor phase with spatially separated graphite in an effectively closed volume under uniaxial pressure (Figure 9). A customized reaction vessel comprising a simple graphite punch and die design was constructed such that uniaxial pressure was applied to the specimen while heated in a tube furnace. To prevent the adhesion between graphite and clathrate crystals, a 1 mm thick layer of dry NaCl powder is introduced between the Na_4Si_4 precursor and graphite. The NaCl layer serves as an effective passive physical barrier to direct reaction between graphite and Na_4Si_4 , but allows diffusive exchange of Na *via* the vapor phase. This C-NaCl- Na_4Si_4 -NaCl-C “sandwich” is encapsulated on all sides by graphite foil to impede the escape of Na vapor, then compressed and clamped under uniaxial pressure of 115 MPa at room temperature. The entire assembly is introduced into a fused silica ampoule, coupled to a vacuum system, evacuated to 10^{-6} torr, and heated at the desired reaction temperature under dynamic vacuum.

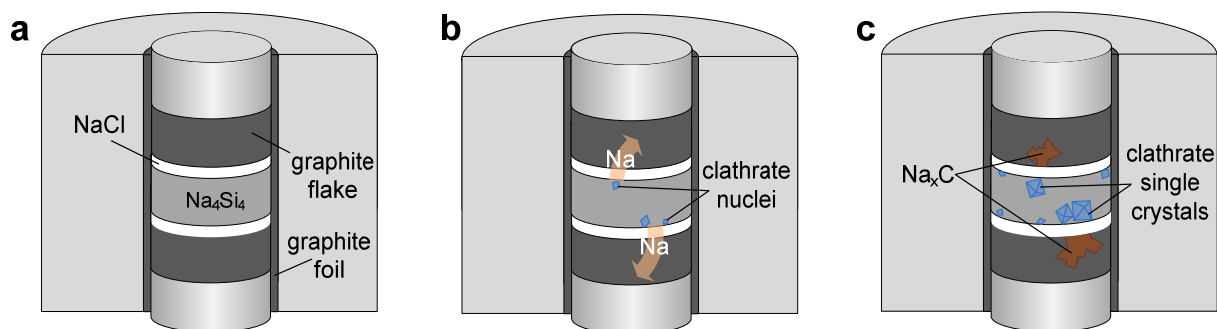


Figure 9. Simple schematic illustrating the Na₈Si₄₆ and Na₂₄Si₁₃₆ crystal growth processes. (a) The initial precursor configuration under uniaxial pressure in the punch and die. (b) Local composition change and nucleation of the clathrate phase. (c) Formation of intercalated graphite and clathrate crystal growth.[35]

The Na vapor, released from the Na₄Si₄ precursor, reacts with the spatially separated graphite, forming intercalation compounds Na_xC. Powder X-ray diffraction of the graphite flake recovered after the reaction confirms the presence of a mixture of stages of Na intercalated graphite. Presumably, the vapor pressure of Na over the intercalated graphite is less than that over Na₄Si₄, such that the intercalation of the graphite results in further release of Na from the precursor in order to locally maintain the Na vapor pressure over the precursor (Le Chatelier's principle). Continued reaction to form Na_xC continuously drives the composition in the precursor Si rich. Nucleation of the respective clathrate phase ensues as the Na content of the sintered body is reduced, and the continuously applied uniaxial pressure facilitates mass transport between precursor and growing crystal. The rate of these dynamic processes is expected to be limited by mass exchange through the vapor phase, as well as diffusion of Na out of the precursor and the reaction kinetics of Na_xC formation.

This approach allowed for selectivity in crystal growth of Na₈Si₄₆ or Na₂₄Si₁₃₆ by merely changing the reaction temperature (Figure 10). Between 580 °C and 590 °C, clathrate-I Na₈Si₄₆ was found to exclusively form, whereas between 660 °C and 670 °C crystal growth of clathrate-II Na₂₄Si₁₃₆ occurred instead.[35] It is noteworthy that direct synthesis and crystal growth of these phases from the elements is unsuccessful, and the available Na-Si equilibrium diagram describes only a eutectic between Na₄Si₄ and Si and the absence of the clathrate phases.[37] Our manuscript describes in detail this approach, as well as the structural data and analyses from single-crystal XRD.[35] Of particular note is the RRR = 36 measured for Na₈Si₄₆ that is several times larger than the highest RRR value previously or since reported for any clathrate compositions, and is evidence of the high quality crystals grown by KCTD.

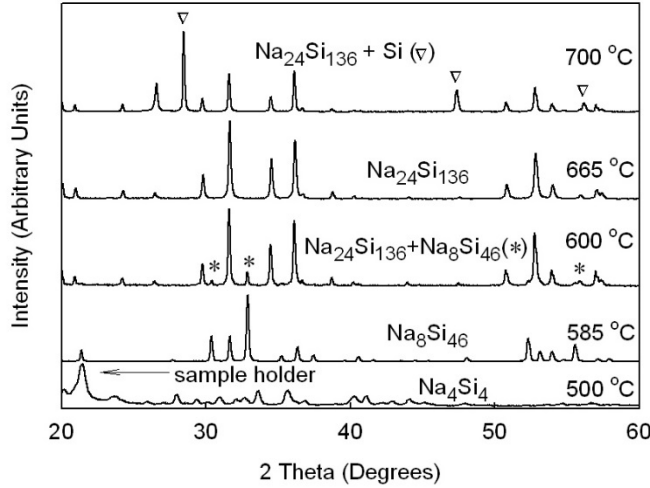


Figure 10. Formation of different phases at different temperatures starting from the same precursor Na_4Si_4 . The single-crystal products were crushed in order to perform powder X-ray diffraction (XRD).

Single-crystal XRD studies and transport properties measurements on several different crystals of $\text{Na}_8\text{Si}_{46}$ and $\text{Na}_{24}\text{Si}_{136}$ resulted in the detailed investigation of the structure and bonding of these materials, their intrinsic low temperature properties, as well as an indication of the reproducibility of our two crystal-growth techniques.[12, 23, 35, 36] The intrinsic properties of both clathrate compositions were revealed for the first time through these analyses. $\text{Na}_{24}\text{Si}_{136}$ is perhaps the best example to illustrate our data and results. The harmonic oscillator model provides a simple yet

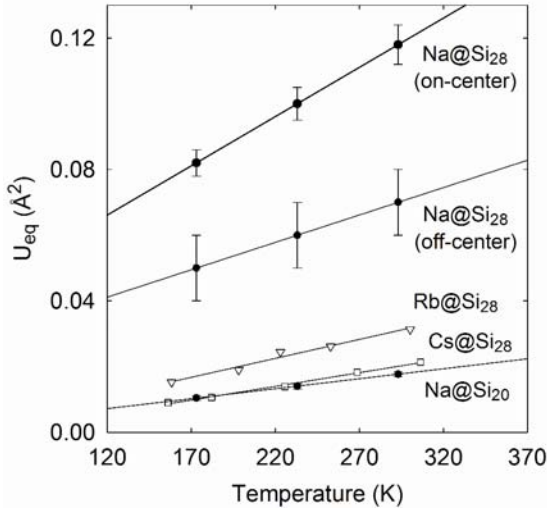


Figure 11. Temperature dependence of the Na U_{eq} obtained from single-crystal XRD, along with those of Cs@Si₂₈ and Rb@Si₂₈. Error bars represent one estimated standard deviation.[38]

useful tool to gain insight from atomic displacement parameter analysis,[25] especially for atomic vibrations that can be approximated by localized Einstein modes. At temperatures such that the Einstein temperature $\Theta_E = h\nu/k_B < 2T$, where ν is the oscillator frequency, h is the Planck constant, and k_B is the Boltzmann constant, the simple classical relation $U_{eq}(T) = k_B T / [m(2\pi\nu)^2]$ can be expected to describe the temperature dependence of the atomic displacement parameter.[25] Fitting the data to this model as shown in Figure 11, we obtain estimated oscillator energies $h\nu$ of

7.2 meV and 16.0 meV for Na@Si₂₈ and Na@Si₂₀, respectively. These results corroborate our inelastic neutron scattering measurements on microcrystalline powders.[38] The value for Na@Si₂₈ is indicative of a low-energy phonon mode associated with Na, and is comparable to rattler energies observed in clathrate-I compounds.[29] A substantial zero-temperature intercept of U_{eq} for Na at the 8b site (Na@Si₂₈) suggests static disorder. An off-centered (positioned at the 32e site, i.e. 4-fold split-site) model [39] was also refined against the single-crystal data. This was corroborated by our extensive powder XRD [35] and x-ray absorption spectroscopic [40] analyses. Although reduced in magnitude, U_{eq} remain relatively large even with the added static disorder. Model density functional theory investigations suggest either a flat, broad potential for Na in the Si₂₈ cage with the minimum in the cage center [31], or a very shallow minimum at approximately 0.5-1.0 Å away from the center.[41] In either case, at elevated temperatures thermal excitation will cause Na to dynamically explore the large volume of the Si₂₈ cage, in agreement with the strong temperature dependence of U_{eq} for Na@Si₂₈. [38]

The intrinsic transport properties measured on single-crystals of Na₂₄Si₁₃₆ grown by SPS,[23] and single-crystals of Na₈Si₄₆ and Na₂₄Si₁₃₆ grown from KCTD [35, 36, 38] serve to illustrate some of the capabilities now available through the use of these two synthetic approaches for the preparation, crystal growth and physical properties characterization of intermetallic clathrates. The key aspect of this work, however, is not only in overcoming the extrinsic effects that were previously unavoidable when consolidating microcrystalline specimens of these compositions, but in the fact that these synthetic approaches affords us the ability to explore key physical concepts associated with the structure-property relationships in intermetallic clathrate materials of differing compositions and “guest” concentrations. The availability of single crystals allows for such exploratory research. In addition, other new and novel materials can be prepared by one or both of these approaches, allowing for the further investigation into compositions with unique properties. An investigation into the structural and transport properties of a series of Na_xSi₁₃₆ specimens is one example.[42]

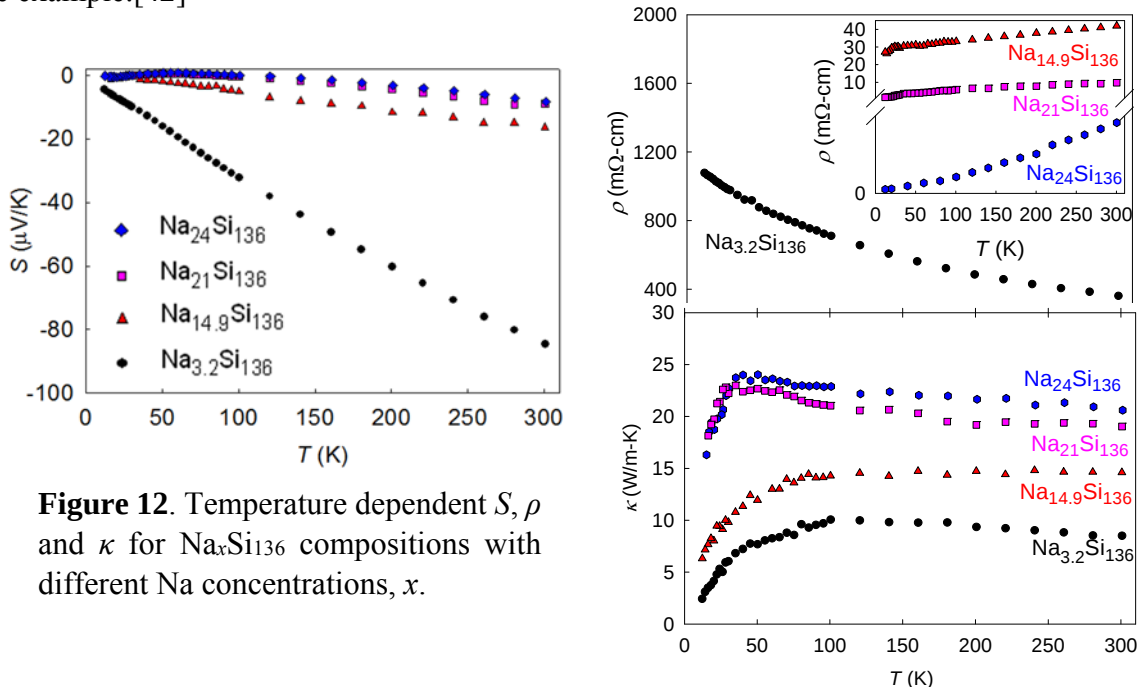


Figure 12. Temperature dependent S , ρ and κ for Na_xSi₁₃₆ compositions with different Na concentrations, x .

Figure 12 shows the temperature dependence of ρ , S and κ for $\text{Na}_x\text{Si}_{136}$. The modulus of S increases with temperature, as expected in metals and heavily doped semiconductors with negligible phonon drag. The relatively low magnitude of S for $\text{Na}_{24}\text{Si}_{136}$ is typical for metals where the location of the Fermi level is well inside the conduction band, as indicated by density-functional theory calculations.[31, 43] As the Na content decreases, the modulus of S increases, reaching a value of 85 $\mu\text{V/K}$ at room temperature for $\text{Na}_{2.9}\text{Si}_{136}$. According to these theoretical studies, the similarity between the density of states profiles for Na (both $3s$ and $3p$) and the total density of states indicates a significant hybridization between metallic Na and the Si framework wavefunctions when Si_{20} are filled. This is consistent with the metallic behavior of $\text{Na}_x\text{Si}_{136}$ for high Na loading. The average Na1-Si and Na2-Si distances decrease as x decreases to 8.2 (Na1 being Na@ Si_{20} and Na2 Na@ Si_{28}). This may imply a significant hybridization between Na and Si corroborating the metallic behavior for $x > 8$. For $x < 8$ however, there are no Na1 which presumably would reduce hybridization.

The temperature dependence of ρ indicates an apparent metal-to-semiconductor transition (Figure 12). There is a clear difference in the magnitude and temperature dependence of ρ as x changes from 2.9 to 24. The ρ values increase with increasing temperature for $x = 8.2, 14.7$ and 24, typical for metals, and decrease with increasing temperature for $x = 2.9$ and 5.1, typical for semimetallic or semiconducting materials. The room temperature ρ value for $\text{Na}_{2.9}\text{Si}_{136}$ is over two orders of magnitude higher than that for $\text{Na}_{14.7}\text{Si}_{136}$, and five orders of magnitude lower than that of the lowest Na content $\text{Na}_x\text{Si}_{136}$ specimens hot pressed from powders.[2, 43] From Quantum Molecular Dynamics studies on Si_{136} and $\text{Na}_4\text{Si}_{136}$ it was shown that Na moves away from the center of Si_{28} by 0.17 Å.[44] From EXAFS studies on $\text{Na}_8\text{Si}_{136}$ [39] a strong interaction between Na2 results in Jahn-Teller distortion and Na2 dimer formation, possibly originating from the spin-spin interactions from the unpaired $3s$ electrons of Na. Our results show that the Na2-Na2 distances decrease as x decreases. The shortest Na2-Na2 distance for $\text{Na}_{24}\text{Si}_{136}$ is 6.01 Å and decreases to 5.90 Å for $\text{Na}_{2.9}\text{Si}_{136}$; therefore, partial covalent bonding between Na2 is more likely to occur at low Na concentrations. This partial covalent bonding between Na2, combined with the weak Na2-Si hybridization that results from the larger Na2-Si distances for $x < 8$, [39, 40, 43] may result in localization of the electrons and ‘drive’ the system to a less metallic state. Similar behavior in the endohedral metallofullerene $\text{Y}@\text{C}_{82}$ has been reported.[45] Our experimental results corroborate prior theoretical work. Semiconducting behavior for $\text{Na}_4\text{Si}_{136}$ was predicted by the first principle full-potential all electron linearized plane wave method.[35] It was suggested that the Jahn-Teller effect lifts the degeneracy at the Γ point and opens a small band gap.[35] In addition, Mott [20] argued that the Na wavefunction overlap decreases as the Na concentration decreases, and the electrons become localized on the Na atoms. When this localization occurs, a Mott transition takes place and the system becomes semiconducting.[20] This is corroborated by the increase in the Na-Si distances for $x < 8$. As Na moves away from the Si framework atoms, there may be less hybridization between Na and Si which results in localization of the electrons around Na. The shortest Na-Na distance (5.1759 Å) excludes the possibility of direct Na-Na interaction, as also suggested by Roy et al.[20] The metal-insulator transition with Na content can clearly be seen from Figure 13.

The thermal conductivities for the five $\text{Na}_x\text{Si}_{136}$ specimens are also shown in Figure 12. The magnitude of κ is relatively large as compared to that of other intermetallic clathrates.[1, 46] The observed κ for $\text{Na}_{24}\text{Si}_{136}$ is higher than the other clathrates shown in Figure 12 due to the fact that

it is dominated by the electronic component.[23] The room temperature values of κ for $\text{Na}_{2.9}\text{Si}_{136}$ and $\text{Na}_{5.1}\text{Si}_{136}$, the two specimens with the lowest Na content, are approximately three times lower than that of $\text{Na}_{24}\text{Si}_{136}$.

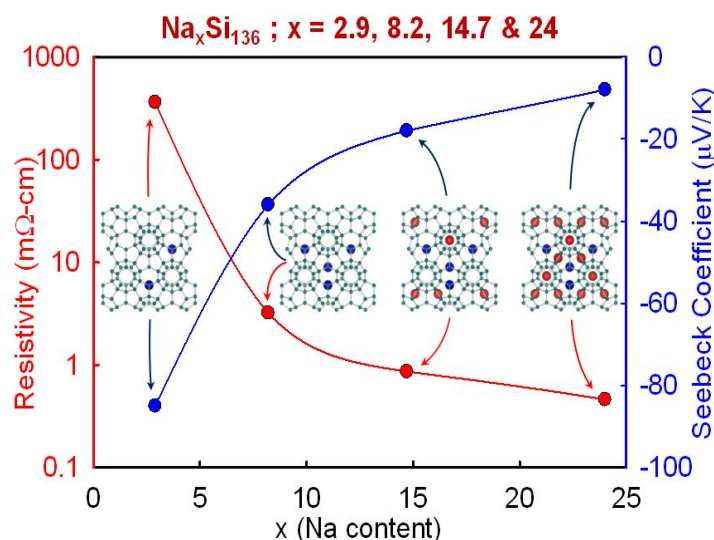


Figure 13. Room temperature S and ρ as a function of Na content, x , clearly showing the metal-insulator transition with Na content for $\text{Na}_x\text{Si}_{136}$. The room temperature transport data is from Figure 12.

Synthesis and structural characterization of single-crystal $\text{K}_{7.5}\text{Si}_{46}$ and $\text{K}_{17.8}\text{Si}_{136}$ clathrates

We can employ KCTD for the selective synthesis of other clathrates, such as $\text{K}_{7.5}\text{Si}_{46}$ and $\text{K}_{17.8}\text{Si}_{136}$ single-crystals.[47] The potassium containing clathrate-II silicon is synthesized unequivocally for the first time, reflecting substantial promise of this approach to obtain novel clathrate-II compositions, of which only a handful are known outside of the work conducted under this project.[1, 46] K_4Si_4 precursor was synthesized by direct reaction of elemental K (Alfa Aesar, 99.98%) and Si (Alfa Aesar, 99%) powder in a K:Si atomic ratio of 1.1:1. The reaction was carried out inside a tungsten crucible that was inside a sealed stainless steel canister at 550 °C for 36 hours. The resulting product was a dark gray crystalline material which was then coarsely ground into powder in a dry nitrogen atmosphere. By maintaining a sufficient partial pressure of the alkali metal over graphite, K was removed from the K_4Si_4 precursor resulting in single-crystal formation. The crystals were synthesized by maintaining the precursor at 550 °C and 625 °C for the clathrate-I and II compositions, respectively, for 15 hours (Figure 14). No change in the precursor was observed at temperatures below 500 °C. Annealing the precursor at temperatures higher than 650 °C and longer than 24 hours lead to the formation of the α -Si phase. The product of the reaction was separated from the unreacted K_4Si_4 by washing with ethanol and distilled water. The $\text{K}_{7.5}\text{Si}_{46}$ crystals formed in relatively uniform cubes 100 – 200 μm in length whereas the $\text{K}_{17.8}\text{Si}_{136}$ crystals form in a pyramidal habit < 100 μm on the longest side. Structural analyses were performed using single-crystal X-ray diffraction. The U_{eq} values indicated no “rattling” for $\text{K}@Si_{20}$ in $\text{K}_{7.5}\text{Si}_{46}$, similar to $\text{Na}@Si_{20}$ in $\text{Na}_8\text{Si}_{46}$. This is in contrast with $\text{K}@Si_{28}$ in $\text{K}_{17.8}\text{Si}_{136}$, where “rattling” was

observed, however not as pronounced as for Na@Si₂₈ in Na₂₄Si₁₃₆.^[47] This research also allowed for an investigation of the intrinsic transport properties of these materials.^[47]

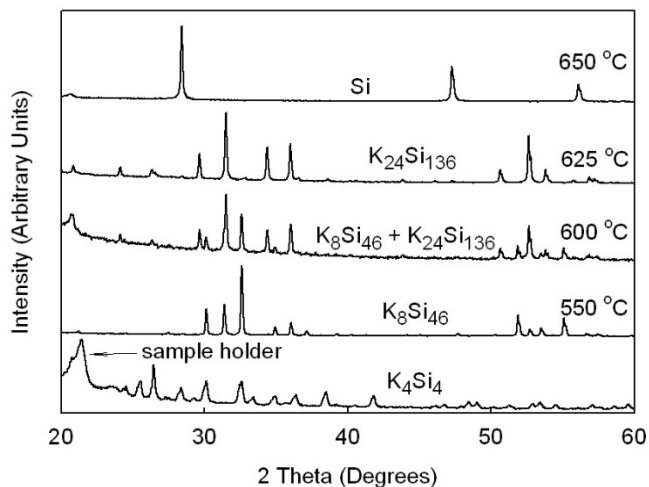


Figure 14. Formation of different phases at different temperatures starting from the same precursor K₄Si₄. The single-crystal products were crushed in order to perform powder XRD.

Spark plasma sintering: Crystal growth optimization

The crystallinity of clathrate-I Na₈Si₄₆ and clathrate-II Na₂₄Si₁₃₆ was also investigated as a function of applied pressure and temperature employing SPS.^[48] Specimens with the clathrate-I and II crystal structures were synthesized by SPS processing of Na₄Si₄ at the respective temperatures of 450 °C and 600 °C, and uniaxial pressures of 60, 80, and 100 MPa for 3 hours. I note that this investigation also revealed the optimum SPS parameters for the selective synthesis of these clathrate compositions. The temperature ramp rates were 100 °C /min for the clathrate-I phase, and 25 °C /min up to 450 °C and then 10 °C /min up to 600 °C for the clathrate-II phase. Selective synthesis was achieved by choosing the appropriate temperature, 450 °C for the clathrate-I phase and 600 °C for the clathrate-II phase. No change in the precursor was observed at temperatures below 400 °C. At 550 °C a mixture of both phases was observed. SPS processing at 650 °C yields the α-Si phase. The highest yield of single crystals was achieved at 450 °C and 600 °C for the clathrate-I and II phases, respectively, at 100 MPa. This approach allowed for the selective-synthesis of single-crystal and microcrystalline Na₈Si₄₆ and Na₂₄Si₁₃₆ as a function of the applied pressure. At 60 MPa high purity microcrystalline products were observed. When the pressure was increased from 60 MPa to 80 MPa, clathrate-II single crystals started to form but clathrate-I single crystals formed at 100 MPa. The average size of the single crystals was obtained from SEM analyses. The average size of the clathrate-I phase does not change as the pressure is increased from 60 to 80 MPa, in contrast to the clathrate-II phase. The average crystal size for the clathrate-II phase at 80 MPa is smaller than that at 100 MPa, suggesting that the crystal size increases with increasing pressure. Table I contains these SPS processing conditions and resulting materials and morphologies.

SPS processing at 60 and 80 MPa resulted in only microcrystalline Na₈Si₄₆, whereas at 100 MPa only single crystals were observed at the appropriate temperatures. The average size of the single-crystal products, 150 μm and 250 μm for the clathrate-I and II phase, respectively, is comparable to that obtained by our other single-crystal synthesis method. At 550 °C and 100 MPa a mixture

of powders and single crystals of both clathrate phases was observed. The relative clathrate fraction in the synthesis product as a function of reaction time was also investigated. When the precursor was reacted at 600 °C for 30 minutes, the clathrate-I phase was estimated to be approximately 60 % whereas the clathrate-II phase was approximately 40%, from powder XRD analyses. As the reaction time increased at the same temperature, the intensity of the clathrate-I reflections in the XRD spectra decreased. For a reaction time of 3 hours only the clathrate-II phase was observed. The average size of Si obtained by SPS processing of the Na₄Si₄ precursor at 650 °C was 65 nm; therefore this approach can also yield nano-sized Si. The high heating rates and localized heating in the SPS, considered two of the most important factors for the synthesis of Si nanoparticles, may be an indication that SPS is also a promising method for the synthesis of Si nanoparticles.

Table I. Processing conditions for SPS synthesis from the precursor Na₄Si₄.

<i>T</i> (°C)	<i>P</i> (MPa)	Phase	Crystallinity	<i>L</i> (μm)
450	60	clathrate-I	microcrystalline	10
	80	clathrate-I	microcrystalline	10
	100	clathrate-I	single crystal	150
550	60	clathrate-I+II	microcrystalline	10
	80	clathrate-I+II	microcrystalline + single crystal	10/150
	100	clathrate-I+II	microcrystalline + single crystal	10/150
600	60	clathrate-II	microcrystalline	15
	80	clathrate-II	single crystal	50
	100	clathrate-II	single crystal	250
650	100	Silicon	nano-crystalline	0.065

SPS can also be successfully employed for the synthesis of the type-I a Si-Ge alloy clathrates. SPS processing of a Na₄(Si,Ge)₄ precursor with a 50/50 Si/Ge molar ratio at 450 °C for one hour resulted in the synthesis of Na₈Ge_{2.8}Si₄₀. The lattice parameter, 10.2133(21) Å, for this composition is slightly larger than that of Na₈Si₄₆. The refined atomic coordinates and U_{eq} values for Na1 and Na2 are much larger than that of the framework atoms, which may be an indication of dynamic disorder of Na inside the polyhedral cavities. U_{eq} for Na2 are relatively large, however they are smaller than those of Na1. Even though Na2 is encapsulated within the larger polyhedron, it exhibits lower U_{eq} as compared to that of Na1. This is due to the vacancies present on the 6c crystallographic sites that presumably result in shrinkage of the size of the larger polyhedra, therefore reducing the available “room” for Na2 to “rattle”. The interstitial 2a and 6d crystallographic sites are fully occupied with Na, and the framework 16i and 24k are fully occupied with Si. The 6c site is partially occupied by Si and Ge. In addition, the Na2 atoms that are typically found to exhibit anisotropic atomic displacement parameters due to the lower symmetry of the larger polyhedral cavities, are now found to be isotropic. This is presumably related to the presence of vacancies at the 6c crystallographic sites which result in distortion of the larger polyhedra. The 6c crystallographic sites are associated with the atoms residing on the hexagonal rings of the larger tetrakaidecahedra. Therefore, the presence of vacancies at the 6c crystallographic site results in an increase of the symmetry of these tetrakaidecahedra, and therefore isotropic ADPs for the Na

atoms encapsulated in their polyhedral cavities. The atomic distances for $\text{Na}_8\text{Ge}_{2.8}\text{Si}_{40}$, obtained from our refinement results, indicate that the Si-Si distances are comparable to those of the $\text{Na}_8\text{Si}_{46}$ and $\text{K}_{7.5}\text{Si}_{46}$ clathrates, whereas the Si-Ge distances are slightly larger than the Si-Si distances presumably due to the larger radius of Ge as compared to Si. This also results in a larger lattice parameter for $\text{Na}_8\text{Ge}_{2.8}\text{Si}_{40}$ as compared to that of the type I clathrates $\text{Na}_8\text{Si}_{46}$ and $\text{K}_{7.5}\text{Si}_{46}$. The larger lattice parameter of $\text{Na}_8\text{Ge}_{2.8}\text{Si}_{40}$ is consistent with the larger Na-Ge distances as compared to the Na-Si distances.

Ionic liquid synthesis

The synthesis of $\text{Na}_8\text{Si}_{46}$ and $\text{Na}_{24}\text{Si}_{136}$ without clathrate impurity phases and in relatively high yield was achieved by oxidation of Na_4Si_4 from the byproduct of the decomposition of the ionic liquid (IL) ndodecyltrimethylammonium chloride (DTAC) combined with AlCl_3 . [49] Unlike previous studies [50, 51] we separate the IL from the precursor in order to avoid secondary clathrate or amorphous phases. [52] The thermal decomposition of the IL supplied the oxidizing agent, mainly HCl. [53] The HCl is further reduced to H_2 as the chloride reacts with the alkali metal anions, forming a stable byproduct, such as NaCl as observed in this study. Maintaining separation of the IL from the precursor together with careful control of the synthetic parameters, temperature and time in particular, allowed for the synthesis of both clathrate structure types without need for further annealing. When the precursor Na_4Si_4 was reacted for a period of 24 hours at temperatures of 210 to 240 °C, the result was the type II clathrate $\text{Na}_{24}\text{Si}_{136}$. Reactions at similar temperatures for 8 hours result in type I clathrate $\text{Na}_8\text{Si}_{46}$ formation. The highest yield of $\text{Na}_{24}\text{Si}_{136}$, 20 % by weight with only α -Si as the impurity phase, was synthesized by reacting at 210 °C for 24 hours. I note that α -Si was always observed in the synthesis of microcrystalline $\text{Na}_{24}\text{Si}_{136}$, and is one of the main reasons that we have developed two new and unique crystal-growth and processing techniques under this project, KCTD and SPS. Nevertheless, phase pure type I clathrate $\text{Na}_8\text{Si}_{46}$ was obtained with a similar yield at 240 °C and a reaction time of 8 hours.

Microcrystalline and single crystal $\text{Na}_8\text{Al}_8\text{Si}_{38}$ synthesized for the first time

A mixture of Na_4Si_4 and NaAlSi was used as the precursor for SPS and KCTD synthesis of $\text{Na}_8\text{Al}_8\text{Si}_{38}$. [54] This composition is of particular interest for potential thermoelectric applications, and has until now not been successfully synthesized. Single crystals of $\text{Na}_8\text{Al}_8\text{Si}_{38}$ were grown by the KCTD technique, while microcrystalline powders were synthesized by SPS processing (Figure 15). Reaction of Na_4Si_4 and NaAlSi with a mole ratio of 7.5:8 at 690°C for 9 hours yielded $\text{Na}_8\text{Al}_8\text{Si}_{38}$. Our refinement results indicated a lattice parameter of 10.3241(7)Å, larger than that of $\text{Na}_8\text{Si}_{46}$ (10.1962(9)Å) as expected due to the larger atomic size of Al ($r = 1.43\text{Å}$) as compared with Si ($r = 1.17\text{Å}$). This reaction process can be thought of as the equilibrium reaction $7.5\text{Na}_4\text{Si}_4 + 8\text{NaAlSi} \rightarrow \text{Na}_8\text{Al}_8\text{Si}_{38} + 30\text{Na}$. The Na vapor phase is gradually absorbed by the graphite layer, therefore the reaction constantly advances toward the synthesis of $\text{Na}_8\text{Al}_8\text{Si}_{38}$. This approach allows for the slow release of Na in the vapor phase which then allows for the reaction to take place at higher temperatures providing adequate energy for the formation of $\text{Na}_8\text{Al}_8\text{Si}_{38}$. This may explain why the synthesis of $\text{Na}_8\text{Al}_8\text{Si}_{38}$ has not been previously reported, although attempted often by different synthetic techniques including high pressure techniques. Using a molar ratio of 7.5 Na_4Si_4 to 8 NaAlSi , $\text{Na}_8\text{Al}_8\text{Si}_{38}$ was synthesized at any temperature between 620 to 720 °C. This represents a much wider temperature range compared to $\text{Na}_8\text{Si}_{46}$ (pure phase $\text{Na}_8\text{Si}_{46}$ forms between 580 and 590 °C). On the other hand pure $\text{Na}_8\text{Al}_8\text{Si}_{38}$ can be obtained even when the annealing time is prolonged to 48h. These results indicate the high thermal stability of $\text{Na}_8\text{Al}_8\text{Si}_{38}$.

Single crystals of $\text{Na}_8\text{Al}_8\text{Si}_{38}$ were grown by the KCTD technique. The precursor, a NaAlSi / NaSi mixture, was placed in custom designed stainless steel tooling under a uniaxial pressure of 20 MPa and heated at 953 K for 9h under a dynamic vacuum of 10^{-6} Torr and phase pure $\text{Na}_8\text{Al}_8\text{Si}_{38}$ in the form of single-crystals was obtained. The UV/Vis diffuse reflectance spectrum (Figure 16) indicates an optical band gap of 0.64 eV, similar to that of the theoretical indirect gap of the hypothetical guest free Si_{46} (0.7 eV) and $\alpha\text{-Ge}$ (0.74 eV). The band gap originates mainly from transitions involving filled $3s$ and $3p$ of Al and Si hybridizations in the valence band and empty Al and Si $3s$ and $3p$ hybridizations in the conduction band. The contributions from Na ions near the Fermi levels can be expected to be minimal due to their strong ionic bonding character with the $\text{Al}_8\text{Si}_{38}$ framework. Consequently, the band gap is determined by the $\text{Al}_8\text{Si}_{38}$ framework. This is presumably why the band gap of $\text{Na}_8\text{Al}_8\text{Si}_{38}$ is similar to that reported for $\text{K}_8\text{Al}_8\text{Si}_{38}$ using density functional calculations.[55]

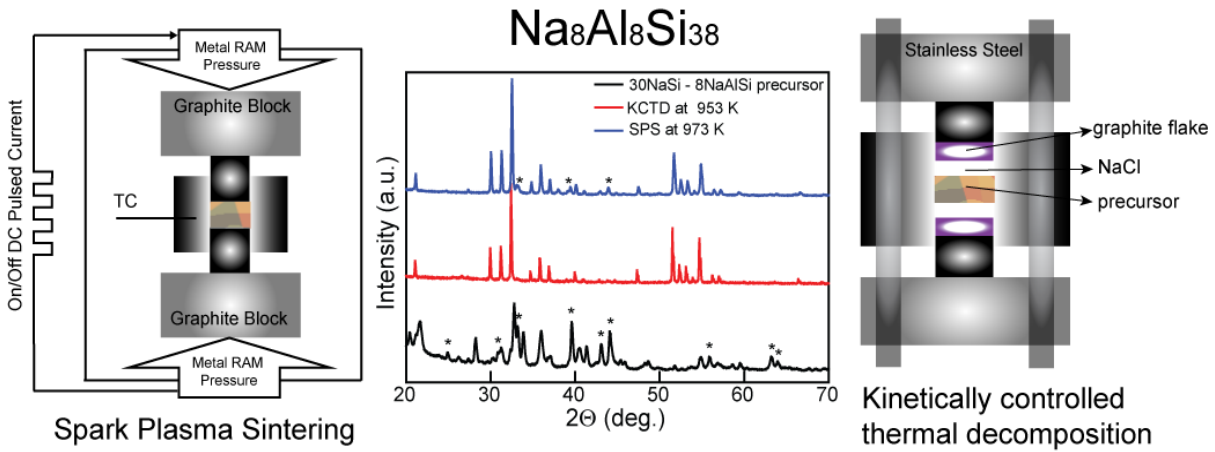


Figure 15. The novel synthetic techniques developed under this DOE project have been employed in processing new multinary clathrate compositions that have until now not been obtained, and therefore also allowed for the investigation of their physical properties for the first time. Both SPS and KCTD have been employed in the synthesis of the ternary intermetallic clathrate $\text{Na}_8\text{Al}_8\text{Si}_{38}$ using a mixture of Na_4Si_4 and NaAlSi as the precursor.[54]

As shown in Figure 17, the electrical conductivity, σ , and modulus of S values increase with increasing temperature. The negative S values throughout the entire measured temperature range, 300 to 500 K, implies electron conduction. The increase in σ with temperature was very small, as is typical for thermally activated semiconductor behavior. The room temperature S value ($-22 \mu\text{V/K}$) was smaller than that of $\text{A}_8\text{Al}_8\text{Si}_{38}$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) and comparable to that of other Al containing clathrate-I compounds such as $\text{Ba}_8\text{Al}_{14}\text{Si}_{31}$ ($-21 \mu\text{V/K}$) and $\text{Ba}_8\text{Al}_{16}\text{Si}_{30}$ ($-48 \mu\text{V/K}$).[54] The measured κ decreases with increasing temperature, typical of dielectric behavior. The room temperature κ value (2.0 W/mK) was slightly larger than that of $\text{A}_8\text{Al}_8\text{Si}_{38}$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) presumably due to the higher σ value, but much smaller than $\text{Na}_8\text{Si}_{46}$.

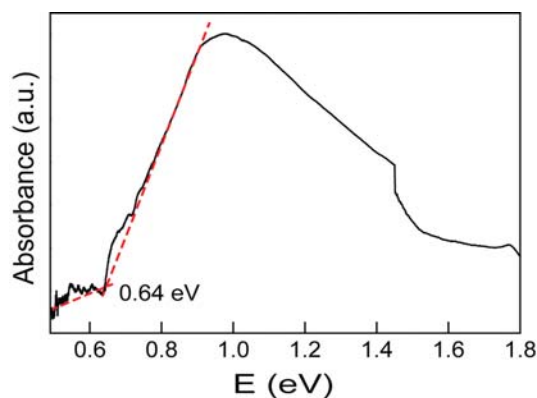


Figure 16. Solid-state UV / Vis absorption spectra of $\text{Na}_8\text{Al}_8\text{Si}_{38}$. A value of 0.64 eV is obtained from the intersection of the fitted base line and absorption edge (red dotted line).

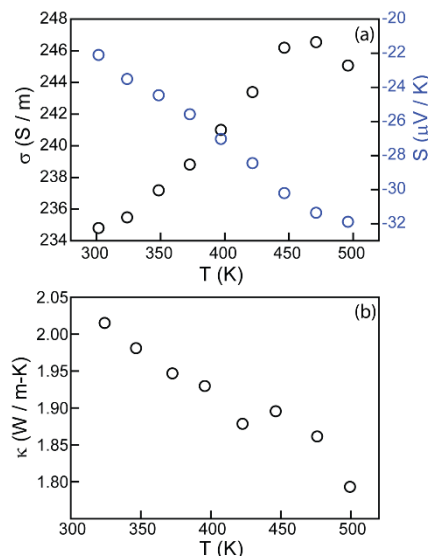


Figure 17. Temperature-dependent (a) σ (black circles) and S (blue circles), and (b) κ for $\text{Na}_8\text{Al}_8\text{Si}_{38}$.

The refined unit cell parameters and bond distances of $\text{Na}_8\text{Al}_8\text{Si}_{38}$ are larger than those of $\text{Na}_8\text{Si}_{46}$ ($a = 10.1962(9)$ Å) [36] due to the inclusion of Al on the framework, but smaller than those of $\text{A}_8\text{Al}_8\text{Si}_{38}$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) [55, 56] and $\text{Ba}_8\text{Al}_8\text{Si}_{38}$ [57] due to the smaller ionic size of the encapsulating Na atoms. Indeed, a plot of the lattice parameter versus ionic radii (coordination number CN = 12) [58] for $\text{A}_8\text{Al}_8\text{Si}_{38}$ ($\text{A} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{and Ba}$) is relatively well described by a linear relationship (Figure 18).

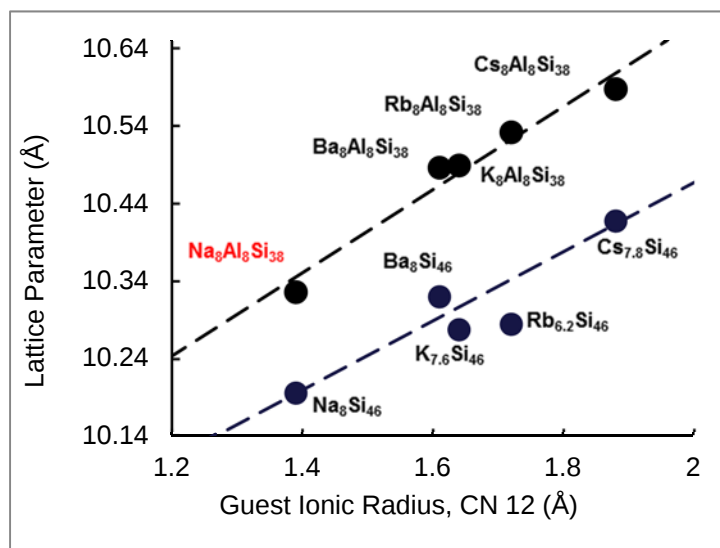


Figure 18. A plot of the lattice parameters versus ionic radii (coordination number CN = 12) of the guest atoms for $\text{A}_8\text{Al}_8\text{Si}_{38}$ ($\text{A} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{and Ba}$) and A_8Si_{46} .

Synthesis and structural characterization of Si-Ge alloy clathrates

A $\text{Na}_4(\text{Si}_{0.9}\text{Ge}_{0.1})_4$ precursor was used to synthesize single crystal type-II $\text{Na}_{24}(\text{Si}_{0.9}\text{Ge}_{0.1})_{136}$ by KCTD for the first time. Large single crystals of nominal composition $\text{Na}_{24}(\text{Si}_{0.9}\text{Ge}_{0.1})_{136}$ were successfully grown at 665 °C for 9 hours. As is the case for $\text{Na}_{24}\text{Si}_{136}$, the $\text{Na}_{24}(\text{Si}_{0.9}\text{Ge}_{0.1})_{136}$ single crystals form in polyhedral shapes, the largest being approximately $0.2 \times 0.2 \times 0.2 \text{ mm}^3$ in size. The $\text{Na}_{24}(\text{Si}_{0.9}\text{Ge}_{0.1})_{136}$ phase can also be synthesized at lower temperatures, however the crystal size decrease with decreasing reaction temperature. Energy dispersive X-ray spectroscopic (EDX) analysis was used to investigate the single crystals and consistently indicated that Ge was present in the crystals.

Both traditional thermal decomposition and KCTD were employed for Si-Ge alloy clathrate synthesis with $\text{K}_4(\text{Si}_{1-x}\text{Ge}_x)_4$ as precursors.[59] $\text{K}_4(\text{Si}_{1-x}\text{Ge}_x)_4$ alloys were synthesized by reacting elemental potassium and ball milled $\text{Si}_{1-x}\text{Ge}_x$ alloys, in a 1.4: 1 molar ratio, at 668 K for 24 h under flowing Ar. The precursor synthesis technique employed in this work was relatively simple and achieved without need of sealed crucibles. $\text{K}_4(\text{Si}_{1-x}\text{Ge}_x)_4$ with $x = 0.1, 0.3$, and 0.75 were heated to 823 K for 8h, 803 K for 8h, and 758 K for 5h, respectively, to obtain type-I alloy clathrates. The final clathrate compounds were stable in air. The phase purity and crystal structure of the specimens were determined by XRD at room temperature. The Si-to-Ge ratios of the clathrate phases were closer to that of the precursors and the site occupancy for the Si/Ge framework followed the same trend as that exhibited by the clathrates prepared by thermal decomposition. The highest Ge content clathrate, $\text{K}_{7.6}\text{Si}_{14.9}\text{Ge}_{31.1}$, contained amorphous Ge. The lattice constants obeyed Vegard's law, exhibiting a linear increase with increasing germanium content. The two compounds with vacancies on the $2a$ site deviated only slightly from Vegard's law.

The phase purity and crystal structure of the specimens were determined by powder X-ray diffraction (XRD) at room temperature. The Si-to-Ge ratios of the clathrate phases are closer to that of the precursors and the site occupancy for the Si/Ge framework follows the same trend as that exhibited by the clathrates prepared by thermal decomposition. The highest Ge content clathrate, $\text{K}_{7.6}\text{Si}_{14.9}\text{Ge}_{31.1}$, contained amorphous Ge. The lattice constants with Ge concentration for all clathrates compounds are shown in Figure 19 and obey Vegard's law, exhibiting a linear increase with increasing germanium content. The two compounds with vacancies on the $2a$ site deviate only slightly from Vegard's law.[59]

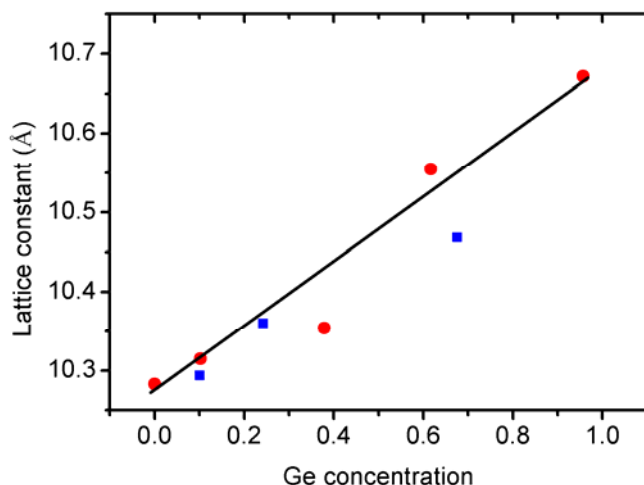


Figure 19. Lattice constant as a function of Ge concentration for the clathrates prepared by thermal decomposition (red) and KCTD (blue).

Investigations of new synthetic route for the preparation of clathrate-II compositions

As described above, an electrochemical redox reaction initiated by the applied electric current that passes through the specimen during SPS processing induces crystal growth, with the Na_4Si_4 precursor acting like a solid electrolyte with sodium transport toward the cathode. We also demonstrated that the selective synthesis of binary Na-Si clathrate-I and -II compositions was possible by changing the applied SPS conditions. It is well known that pure alkali metals such as K, Rb, and Cs can be obtained by ion-exchange employing their chlorides (ACl with $\text{A} = \text{K}, \text{Rb}, \text{Cs}$) with Na at high temperatures. We hypothesized that combining these two approaches will lead to a simultaneous electrochemical redox reaction together with an ion-exchange reaction. When combining Na_4Si_4 together with ACl , the tetrahedral Si_4^{4-} units from the Na_4Si_4 precursor start to oxidize to form the clathrate framework at the anode while elemental Na is formed by reduction of the Na^+ ions at the cathode. During this process Na also reacts with ACl to form NaCl allowing A to be available for encapsulation in the resulting polyhedra of the clathrate framework. Using this knowledge, we also successfully synthesized three clathrate-II compositions ($\text{A}_8\text{Na}_{16}\text{Si}_{136}$), as shown in Figure 20, investigated the synthesis of new compositions employing this approach, and selectively synthesized ternary clathrate-I and II compositions with SPS processing temperature.[60]

Single crystals of three type-II clathrates, $\text{K}_{5.8(1)}\text{Na}_{16}\text{Si}_{136}$, $\text{Rb}_8\text{Na}_{16}\text{Si}_{136}$, and $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$, were synthesized by SPS for the first time.[60] The NaSi precursor along with each alkali-metal chloride were ground together in a 1:1 mass ratio. Pulsed DC current was sourced through the precursor mixture and die assembly while under a uniaxial pressure of 100 MPa in a vacuum of 10 mTorr. The dwell time at the desired temperature (873 K for $\text{K}_{5.8(1)}\text{Na}_{16}\text{Si}_{136}$, 838 K $\text{Rb}_8\text{Na}_{16}\text{Si}_{136}$, and 773 K for $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$) for each reaction was 1.5 hr. The product of each reaction was separated from any unreacted NaSi and ACl by washing with ethanol and distilled water. The U_{eq} values of Rb in $\text{Rb}_8\text{Na}_{16}\text{Si}_{136}$ and Cs in $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$ are relatively small with $U_{eq} = 0.0296 \text{ \AA}^2$ and $U_{eq} = 0.0168 \text{ \AA}^2$, respectively, and very similar to those previously reported. The potassium atoms in $\text{K}_{5.8(1)}\text{Na}_{16}\text{Si}_{136}$ have room temperature atomic displacement parameter values that are 2 to 3 times larger ($U_{eq} = 0.0695 \text{ \AA}^2$) implying that the K atoms partially occupy the Si_{28} polyhedra while possessing a more dynamic disorder inside the Si_{28} polyhedra, as compared with that of Rb and Cs in the other clathrates, due to its relatively smaller ionic size.

Crystal growth by SPS is influenced by the pulsed DC current; however, in the present case an electrochemical redox reaction occurs simultaneously with an ion-exchange reaction. Considering that the reaction occurs completely, we postulate that the reaction process is as follows: $136 \text{ NaSi} + 8 \text{ ACl} \rightarrow \text{A}_8\text{Na}_{16}\text{Si}_{136} + 8 \text{ NaCl} + 112 \text{ Na}$. Here tetrahedral Si_4^{4-} units from the NaSi precursor start to oxidize to form Si_{136}^{24+} at the anode while elemental Na is formed by reduction of Na^+ ions at the cathode through an electrochemical redox reaction. During this process Na^+ ions also react with ACl to form NaCl allowing K, Rb or Cs, together with the remaining Na atoms, to be available for encapsulation in the resulting polyhedra of the clathrate framework. Our results also indicated that reaction time does not substantially affect the yield or size of the single crystals. This approach can also be employed for the synthesis of other compositions; the polycrystalline ternary silicide compound Li_3NaSi_6 was synthesized by this approach when using LiCl and NaSi mixtures as the precursor.

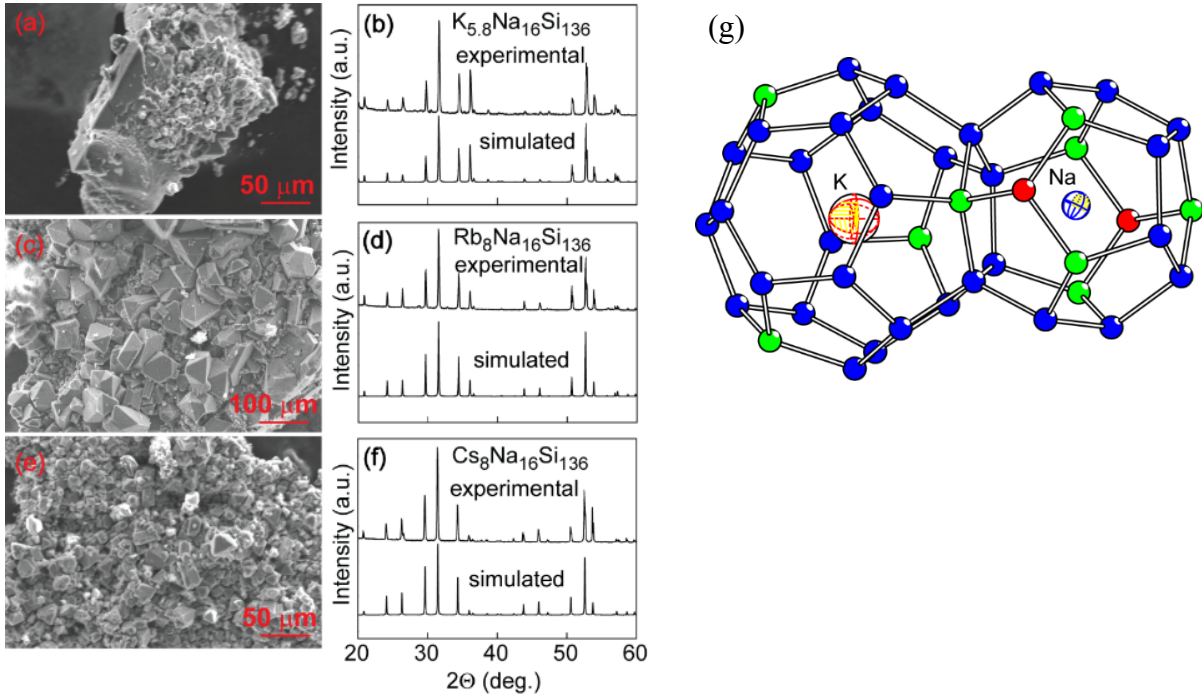


Figure 20. SEM images of the clathrate single crystals and powder XRD patterns from crushed single crystals for (a) and (b) $\text{K}_{5.8(1)}\text{Na}_{16}\text{Si}_{136}$, (c) and (d) $\text{Rb}_8\text{Na}_{16}\text{Si}_{136}$, and (e) and (f) $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$, along with their simulated powder patterns. (g) Hexakaidekahedron (Si_{28}) and dodecahedron (Si_{20}) with corresponding alkali metal atoms in $\text{K}_{5.8(1)}\text{Na}_{16}\text{Si}_{136}$. Thermal ellipsoids for K (8b) and Na (16c) are 90 % probability. Blue, green, and red atoms indicate Si on the 96g, 32e, and 8a crystallographic sites, respectively.

Clathrate-II $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$ synthesized and low temperature transport

We synthesized a quaternary intermetallic silicon clathrate-II compound by KCTD by employing a precursor that was a mixture of NaSi and NaAlSi together with the alkali metal halide CsCl, in effect, a multiprecursor ion exchange synthetic approach (Figure 21).[61] This is the first time a clathrate-II Al-Si framework composition was reported. Structural refinement indicates full occupancy of the framework and that Cs and Na reside at the crystallographic 8b and 16c sites, respectively. The framework bond distances, as well as powder XRD refinement and elemental analysis, indicate that Al atoms were present on the framework sites. Transport properties, investigated from 12 to 300K, and solid state UV-Vis diffuse reflectance measurements show semimetallic behavior with electron conduction. The modulus of S increases linearly with increasing temperature throughout the measured temperature range while the ρ values increase with increasing temperature above 75 K. The measured room temperature S ($-32 \mu\text{V/K}$) is smaller than that of $\text{A}_8\text{Al}_8\text{Si}_{38}$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) but comparable to that of other Al containing clathrate-I compounds such as $\text{Na}_8\text{Al}_8\text{Si}_{38}$ ($-22 \mu\text{V/K}$), $\text{Ba}_8\text{Al}_{14}\text{Si}_{31}$ ($-21 \mu\text{V/K}$) and $\text{Ba}_8\text{Al}_{16}\text{Si}_{30}$ ($-48 \mu\text{V/K}$).[61] Although our refinement and EDS results do not allow us to quantify the aluminum content precisely, our electrical transport data suggest that the Al content is less than the target $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$ content. Semiconducting behavior is expected for $\text{Cs}_8\text{Na}_{16}\text{Al}_{24}\text{Si}_{112}$, from simple

crystal chemistry arguments, however deviation from this stoichiometry will result in a metallic S and ρ temperature dependence. The measured κ values increase up to 200 K after which point they decrease with increasing temperature. This behavior is similar to that of $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$ and $\text{Na}_{24}\text{Si}_{136}$, although our κ values are much smaller than that of these two compositions. Our results indicate that the KCTD synthetic method can be employed for the synthesis of multinary inorganic clathrate phases that cannot be accessible by traditional crystal growth techniques.

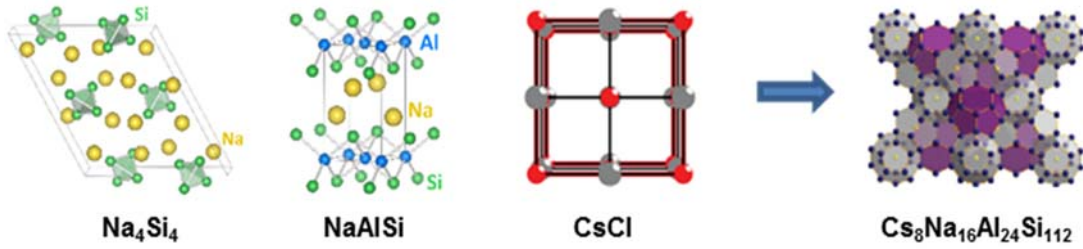


Figure 21. Schematic illustration of the multi-precursor, ion-exchange approach for processing quaternary clathrate-II compositions employing KCTD.

Clathrate-II (K,Ba)₁₆(Ga,Sn)₁₃₆ synthesized and densified employing SPS

Tin clathrate-II framework-substituted compositions are of current interest as potential thermoelectric materials for medium-temperature applications. Potassium and barium filled, gallium framework substituted tin clathrate-II single crystals were synthesized in large quantities so that they may be ground to fine powder for densification employing optimized SPS parameters to form dense bulk polycrystalline specimens for high temperature transport properties measurements.[62] To prepare the specimens, the elements with an excess of Ga and Sn relative to the appropriate stoichiometric ratios were loaded into a tungsten crucible that was then sealed inside a custom-designed stainless steel vessel, with all synthetic procedures occurring inside a nitrogen glovebox. The stainless steel vessel was then transferred into a glass tube and sealed under vacuum. The glass tube was put into a furnace at 923 K for 15 h, followed by slow cooling to 723 K at a rate of one degree per minute before being air cooled to room temperature. The products of this reaction included clathrate-II (K,Ba)₁₆(Ga,Sn)₁₃₆, clathrate-I (K,Ba)₈(Ga,Sn)₄₆, BaSn_3 , Ba_5Sn_3 , Ba_2Sn , as well as elemental Sn and Ga. A mixture of 10 mL HCl, 10 mL HNO_3 , and 80 mL DI water was used to remove this remaining flux from the resulting products, thus allowing for easy separation of the clathrate-II crystals from the other phases.

Our PXRD refinement results indicated a mixed occupancy in the (Ga,Sn)₂₀ dodecahedra, vacant (Ga,Sn)₂₈ hexakaidecahedra, and no vacancy on the framework. This type of preferential polyhedral occupancy can be related to the relative sizes of the constituent atoms. Transport properties of the specimens were investigated from 12 to 300K.[62] The temperature-dependent S data indicates possible bipolar diffusion. The ρ trends somewhat with composition, $\text{K}_{2.9(4)}\text{Ba}_{13.1(2)}\text{Ga}_{23.2(3)}\text{Sn}_{112.7(5)}$ possessing lower ρ values in the measured temperature range as compared with $\text{K}_{7.1(2)}\text{Ba}_{8.8(3)}\text{Ga}_{25.1(4)}\text{Sn}_{110.8(3)}$, which showed more semiconducting-like behavior. This is expected, given the simple chemical analysis whereby each Ga acts as an acceptor for each

donated electron from K^+ and Ba^{2+} . Room temperature Hall measurements indicated carrier concentrations of $3.1 \times 10^{19} \text{ cm}^{-3}$ and $6.2 \times 10^{19} \text{ cm}^{-3}$ for $K_{7.1(2)}Ba_{8.8(3)}Ga_{25.1(4)}Sn_{110.8(3)}$ and $K_{2.9(4)}Ba_{13.1(2)}Ga_{23.2(3)}Sn_{112.7(5)}$, respectively, values that are in the same order-of-magnitude as that of previous reports on clathrate-II Sn compositions. From our measured room temperature carrier concentration and S values, and assuming a simple parabolic band model, we estimated effective mass, m^* , of the two specimens to be $0.45m_e$ and $0.51m_e$ for $K_{7.1(2)}Ba_{8.8(3)}Ga_{25.1(4)}Sn_{110.8(3)}$ and $K_{2.9(4)}Ba_{13.1(2)}Ga_{23.2(3)}Sn_{112.7(5)}$, respectively. A plateau in the ZT values at higher temperatures was observed for both specimens, with the highest ZT value (0.6) achieved for $K_{2.9(4)}Ba_{13.1(2)}Ga_{23.2(3)}Sn_{112.7(5)}$ at 575 K.

Type-II clathrate with a Li-Ge framework synthesized and characterized for the first time

The first intermetallic type-II clathrate phase with Li-substituted framework $Na_{16}Cs_8Li_xGe_{136-x}$ was obtained with composition $x \approx 2.8$ by reaction of the elements at 650 °C.[63] The phase composition was established from crystal structure refinement supported by NMR spectroscopy, microstructure and chemical analyses. In the type-II clathrate crystal structure (space group $Fd\bar{3}m$), Li atoms substitute Ge atoms at site 96g. This may be rationalized by the *Zintl* concept with the formation of tetrahedral $[LiGe_4]^{3-}$ units constituting 3-electron acceptors that compensate a part of the excess electrons from Na and Cs and provide a favorable coordination environment for Li atoms. Due to the somewhat shorter Li-Ge bonding distance compared to Ge-Ge, the lattice parameter of the new quaternary phase is smaller by about 0.2 % than that of the ternary prototype $Cs_8Na_{16}Ge_{136}$ clathrate. From the observed NMR Knight shifts for 7Li , ^{23}Na and ^{133}Cs it is evident that $Cs_8Na_{16}Li_xGe_{136-x}$ ($x \approx 2.8$) is metallic. Comparison of NMR results and magnetic susceptibility with the ternary $Cs_8Na_{16}Ge_{136}$ clathrate and literature data suggest that there is specific electronic interaction of Cs with the $[LiGe_4]^{3-}$ framework entities. Although a number of details on the homogeneity range and interatomic interaction, and their impact on the physical properties, are as yet to be investigated, the successful preparation of $Cs_8Na_{16}Li_xGe_{136-x}$ is a unique framework substitution by Li in clathrate-II compositions. As effectively a 3-electron acceptors, framework-substitution by Li atoms provides a versatile and inexpensive alternative to the (quasi) isoelectronic metals for the preparation of charge-compensated semiconducting intermetallic clathrates that are of potential interest for a variety of technological applications.

Bulk polycrystalline materials with nano-scale grains via SPS

Systems with reduced dimensions have shown superior thermoelectric performance. However, utilizing such materials for practical applications may be challenging. The manufacture of thermoelectric devices requires materials in large quantities, a key reason why device-level development is currently difficult to achieve for superlattice and nanowire materials. Therefore, the dimensional integration of bulk thermoelectric materials with nanoscale features resulting in ZT ($=S^2/\rho\kappa$) enhancement has been in the spotlight as a viable route for increasing ZT . By employing SPS our group has demonstrated that carefully engineered nanostructured materials can result in enhanced thermoelectric performance as compared to their bulk counterparts. Moreover, nano-structured bulk polycrystalline compositions, particularly materials that have relatively low decomposition temperatures, were prepared through bottom-up processing and densified using SPS in order to investigate their transport and thermoelectric properties.[64-67] For all the specimens that have been investigated, κ was greatly reduced due to smaller average grain size and therefore significant grain-boundary phonon scattering. These results demonstrate that bottom-up synthesis followed by optimized SPS processing can result in dense polycrystalline thermoelectric

materials, and is a powerful approach for physical properties investigations of materials with nano-scale grains or inclusions.

Conclusions

One key aspect of this research was the development of new synthetic approaches that allow for an investigation of novel clathrate materials for the first time. Typically, new materials or compositions of scientific or technological importance cannot be synthesized by well-known or established approaches. For such materials new synthetic approaches are required. This work establishes new approaches demonstrating that field-assisted (employing spark plasma sintering, SPS) and kinetically controlled thermal decomposition (KCTD) techniques can be employed for the synthesis of compounds that otherwise cannot be synthesized. These new techniques added to the more established crystal growth and microcrystalline synthetic approaches allowed for the investigation of the physical properties of a variety of new clathrate compositions and structure types. A wide range of physical properties measurements were employed in order to fully characterize the structure, chemical, electrical and thermal properties of the materials developed, synthesized and investigated in this research project. The techniques described in this report can be employed for the synthesis and crystal growth of other intermetallic or metastable compounds. It is clear that these results will greatly aid the scientific community in expanding the knowledgebase of potential clathrate compositions, and potentially further the advance of these materials for technological applications.

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Publications under this project (46 journal articles, one book, and three book chapters)

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