Clathrate Thermoelectrics

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1. Introduction

The term “clathrate” originates from the Latin word for lattice, *clathri*, and the term *clathratus* which means “protected by a cross bar”. The term *clathratus* can be found in the Latin names of several animals, including sea snails and beetles which display elaborate lattice textures and markings, i.e. *boreotrophon clathratus* and *bassareus clathratus*. In biochemistry, a protein called Clathrin adopts a variety of polyhedral shapes and it is an essential component for the formation of vesicles within a cell. Likewise, a unique biological representative of clathrate cages is the *Clathrus Ruber* fungus which is indigenous to Europe (Figure 1.1). The red polyhedral cage-like body of this fungus resembles the basic polyhedral building blocks of the crystalline compounds known as clathrates. Crystalline clathrates have the distinctive structural motifs of the three-dimensional host frameworks which contain a variety of polyhedral cages, and encapsulate guest atoms, ions, or molecules. In these structures, encapsulated guests are not connected to their host frameworks by any strong chemical bonds. Due to the presence of multiple sublattices, clathrates are often classified as either host-guest or inclusion compounds.

Figure 1.1. A photograph of the *Clathrus Ruber* fungus, courtesy of Carol Knudsen.

The chemical term “clathrate” was introduced by *Powell* in 1948 to describe the hydrates which featured guest atoms or molecules trapped in the large cages of their ice-like hydrogen-bonded water frameworks [Powell1948]. The first scientific report of the formation of clathrates was published by *Humphry Davy* in 1811 [Davy1811] in which chlorine gas was passed into cooled water. 140 years later, different models for the crystal structure of chlorine hydrate were proposed by *Pauling* and others [Pauling1952], but it wasn't until 1959 when *Allen* determined the first clathrate crystal structure, that of a chlorine clathrate hydrate [Allen1959]. Just six years later, the first discovery of an inorganic clathrate was made: polar intermetallic Na-Si clathrates were synthesized and structurally characterized [Kasper1965, Cros1965].

Thereupon, many other compounds were reported which contained covalently-bound frameworks of elements from periods 3 through 6 of the Periodic System, encasing either cationic or anionic guests. This remarkable class of compounds, which we will refer to as “inorganic clathrates”, attracted the attention of many solid state chemists and condensed matter physicists due to its unique and elaborate crystal structures and diverse physical properties. While the crystal structures of clathrate hydrates and inorganic clathrates are topologically similar, the principal difference between them is the type of host-guest interactions they involve: weak van der Waals interactions in the case of hydrates and ionic bonding in the case of inorganic clathrates. It should be noted that other terms are also used for this class of compounds to differentiate them from the hydrates, including: semiconducting clathrates, intermetallic clathrates, and Zintl clathrates. Roughly 30 years ago, inorganic clathrates did not have many applications and they were not much more than novelties. Today, however, they are a promising class of materials for a variety of high profile applications, including: thermoelectrics, superconductors, and Li-ion batteries. Several other reviews have been published, describing various aspects of the chemistry and physics of inorganic clathrates [Christensen2010, Beekman2008, Bobev2000b, Kovnir2004b, Shevelkov2011, Nolas2014].

Some of the work from the last half of a century of inorganic clathrate research is summarized in the current review, the focus of which is to describe structure-properties relationships of inorganic clathrates with special attention devoted to thermoelectric properties. Despite the broad focus of this review, it by no means endeavors to cover all aspects of clathrate knowledge. In the following Chapters 2 and 3, the crystal chemistry of clathrates is discussed. Stability and size trends are introduced in Chapter 4, and in Chapter 5, charge balancing via Zintl count is introduced for many of the known clathrate types. Common synthetic methods for clathrates, superstructural ordering, and non-thermoelectric applications of clathrates are discussed in Chapters 6, 7, and 8, respectively, and a basic introduction into thermoelectrics is provided in Chapter 9. The heart of the review, Chapter 10, provides a comprehensive examination and analysis of the available literature data for the thermoelectric properties of clathrates. Trends in these properties are established, related, and explored throughout the chapter. The unquestionably low thermal conductivities of nearly all clathrates are discussed in Chapter 11, with respect to the rattling of guest atoms in the clathrate cages. Relationships between the Einstein and Debye temperatures, clathrate compositions, and thermal conductivities are drawn from the published literature data of these clathrate properties. Finally, in Chapter 12, future directions of clathrate research are considered.

2. Basic Structural Principles

2.1. Clathrate Polyhedra

In crystallography, a common way to describe a crystal structure is by considering how space can be tiled with polyhedra. In some cases, the structure can be described simply by using only one type of polyhedra, such as is the case for the CaF_8 cubes in fluorite. Most often two or more types of polyhedra are necessary [West2013, Alvarez2005]. Most structures are composed of small polyhedra: cubes, octahedra, tetrahedra, etc., but in some cases much larger polyhedra need to be considered, *viz.* in zeolites and metal-organic frameworks (MOFs). The polyhedra used to describe the structures of MOFs and zeolites are not true chemical polyhedra, since the atoms which are located in the corners of the polyhedra are connected by imaginary lines, not by chemical bonds. In zeolites, their topology is described by polyhedra in which Si atoms are located at the corners, and O atoms are located somewhere outside the polyhedral edges. Clathrates represent a unique class of compounds where atoms situated in the vertices of large polyhedra with at least 12-faces and 20-vertices are connected by chemical bonds corresponding to the polyhedral edges.

Figure 2.1. 3D view, pictograms of the number and types of polyhedral faces, and Schlegel diagrams for the six main types of convex clathrate-forming polyhedra.

The crystallographic question of how to tile space with only one type of polyhedra was formulated and partially answered more than 100 years ago, well before the first X-ray diffraction experiment was conducted [Thomson1887]. The answer is trivial for small polyhedra with few faces, such as cubes and tetrahedra. While the original paper contains the simplest and most symmetrical answer to this question for the case of a truncated octahedron, a more comprehensive answer, covering many other possibilities for 14-faced polyhedra, was reported only recently [Delgado-Friedrichs2005]. Each atom in these proposed frameworks is connected to another 4 framework atoms. Each polyhedron is composed of square and hexagonal faces, some with additional pentagonal faces. The valence bond angles in those polyhedra are quite different from the regular tetrahedral angle of 109.45° . In a more recent theoretical investigation, this strong deviation of valence angles from regular tetrahedral coordination was proposed to be the main reason why frameworks composed of only one type of polyhedra would be unstable when based on tetrel elements (Si, Ge, Sn) [Karttunen2011]. Two types of frameworks, one built from truncated

octahedra and another composed of twisted Kelvin cells [Figures 2.1a and 2.1b], were reported in the crystal structures of AM_2P_4 compounds ($A = \text{Sr, Ba}$, $M = \text{Ni, Cu, Pd}$) [Dünner1990, Johrendt1994, Keimes1995, Dolyniuk2015]. Both phosphorus and late transition metals were shown to be able to tolerate significant tetrahedral distortions, for example, in SrNi_2P_4 the $\angle\text{Ni-P-Ni}$ valence angles are 75.9° [Dolyniuk2015].

Si, Ge, and Sn form polyhedral frameworks which are more complicated in nature, as most of them are composed of two types of polyhedra. The most common polyhedral component is the pentagonal dodecahedron in which the valence angles are 108° , close to ideal tetrahedral angles (Figure 2.1c). This polyhedron exhibits five-fold symmetry, thus it cannot tile space on its own in a periodic fashion. To achieve a periodic arrangement, the dodecahedron has to be combined with a less symmetrical polyhedron made up of 2 to 4 additional hexagonal phases (Figures 2.1d-2.1f). All the clathrate-forming polyhedra shown in Figure 2.1 are Euler polyhedra, for which the equation $N_f + N_v = N_e + 2$ relates the numbers of faces (N_f), vertices (N_v), and edges (N_e). Each polyhedron may be denoted by the number of four-, five-, and six-membered faces, similar to the classification of silicates [Liebau1985]. For instance, the notation $[5^{12}6^2]$ indicates a polyhedron with twelve five-membered faces and two six-membered faces.

It should be noted that the aforementioned polyhedra are not the only possible ways to tile space with square, pentagonal, and hexagonal faced polyhedra [Delgado-Friedrichs2005, Delgado-Friedrichs2010, Sikiric2010, Sikiric2012, Karttunen2011, Karttunen2013]. Among the large variety of computationally-predicted space-tiling patterns, only some of the combinations have been realized experimentally in the structures of clathrate compounds.

2.2. Clathrate classifications

The nomenclature of clathrates comes from the naming of clathrate hydrate compounds [Jeffrey1984]. Water hydrates crystallize in seven basic structure types which are historically numbered with the Roman numerals I-VII. For inorganic clathrates, a few other structure types were discovered which were labeled clathrate-VIII, clathrate-IX, and the clathrate composed of twisted Kelvin cells (Figure 2.1b) is called the twisted clathrate. It should be noted that neither clathrate-VIII nor clathrate-IX are true clathrates from the point of view of space filling. Unlike clathrate types I-VII and the twisted clathrate, in clathrate-related compounds, their polyhedra do not tile all space, and smaller voids are present which can be empty or filled depending on the clathrate type.

The types of polyhedra present in each of the inorganic clathrate structures are listed in Table 2.1 along with relative ratios of the types. As indicated in the second column of Table 2.1, the distribution of reported clathrate compositions over those structural types is uneven. Only clathrates of type I, II, III, and VII were realized in inorganic clathrates, and no clathrates of type IV, V, and VI have been reported so far. In one intermetallic compound, $\text{Li}_{14.7}\text{Mg}_{36.8}\text{Cu}_{21.5}\text{Ga}_{66}$, the Li/Mg framework is similar to the oxygen framework in the hydrate clathrate-IV, but the framework cages are filled with different metal clusters, and strong bonding between those clusters and framework elements occurs [Lin2008]. Due to the completely different bonding picture of this system versus that of a traditional inorganic clathrate, we do not consider this compound to be a true clathrate.

There are several ways to classify clathrates. Based on the framework-forming elements, all clathrates can be divided in four groups: Si-based, Ge-based, Sn-based, and finally the tetrel-free clathrates. The latter group can also be called pnictogen-based or transition metal-based since all of the tetrel-free clathrates reported thus far are formed by a combination of the late transition metals of groups 10-12 with pnictogen atoms, including: P, As, or Sb. However, one can imagine other clathrates in which the framework is built up of additional elements such as those of group 13 and 16. Thus, the tetrel-free term is more appropriate. Up to now, just over 10 tetrel-free inorganic clathrates have been reported. These include phosphides (i.e. $\text{Ba}_8\text{Au}_{16}\text{P}_{30}$, SrNi_2P_4), arsenides ($\text{A}_8\text{E}_{18}\text{As}_{28}$, $A = \text{Rb, Cs}$; $E = \text{Zn, Cd}$), and antimonides ($\text{Cs}_8\text{E}_{18}\text{Sb}_{28}$, $E = \text{Zn, Cd}$) [Fulmer2013, Dolyniuk2015, He2012, Liu2009].

Likewise, clathrates can also be classified according to the formal charges of their frameworks. In this way, all clathrates are classified as anionic, cationic, or neutral. In the anionic clathrates, the framework

bears a formal negative charge and the guest atoms are positively charged. The guests are the cations of alkali, alkaline-earth metals, and rare-earth metals. This group represents 90% of all known inorganic clathrates. The reverse situation is observed in a smaller family of cationic clathrates, where the framework has a formal positive charge and the guest atoms are negatively-charged halide (Cl, Br, I) or chalcogenide (Se, Te) anions. Two examples of clathrates with neutral frameworks (thus, guest-free) were produced by carefully removing the guest cations from an anionic Si clathrate or by the mild oxidation of a suitable Zintl phase precursor which led to empty Ge clathrates [Guloy2006, Ammar2004].

The periodic table shown in Figure 2.2 indicates which elements have been reported as clathrate framework-forming elements (orange) and which have been reported as guest atoms inside the polyhedral cage frameworks (blue). Of all of the elements, Li, Na, Te, and I are unique, as they have been found in both clathrate frameworks and at guest sites inside clathrate cages. Moreover, Te and I form binary compounds with Si and Ge, where they function as both framework and guest atoms in the same clathrate compounds: $[\text{Si}_{44.5}\text{I}_{1.5}]\text{I}_8$, $[\text{Ge}_{43.3}\text{I}_{2.7}]\text{I}_8$, and $[\text{Si}_{38}\text{Te}_8]\text{Te}_8$ [Nesper1986, Reny2000, Jaussaud2004].

The size of the circles in Figure 2.2 provides the relative abundance of each element as a component of clathrates. One can clearly see that the elements of the 2nd period are rarely present in clathrates. Likewise, only a few examples of boron-containing clathrates have been reported [Jung2007, Condrón2008].

Several computational reports have predicted that carbon-containing clathrates should be stable; especially in the structure types of clathrates-I, -II, and -VII [Nesper1993, Blase2010, Zeng2015]. Moreover, extreme hardness and high temperature superconductivity were predicted for these carbon-based clathrates. Unfortunately, no reliable experimental evidence of the existence of carbon-based clathrates has been presented thus far.

Figure 2.2. A periodic table representation showing which elements form inorganic clathrate frameworks (orange) and which are found situated inside the polyhedral cages (blue). Li, Na, Te, and I are special elements which can serve as both guest and framework atoms. The radii of circles indicate the relative abundances of the elements in clathrate compounds.

Table 2.1. A summary of different clathrate types, their symmetry, abundance, and constituent polyhedra. G: guest atom; F: framework atom. Colors of polyhedra are identical to those in Figure 2.1.

Clathrate Type	Approximate Number of Compounds	Space Group	Ideal Formula	Polyhedra Types and Ratios		
I	~200	$Pm\bar{3}n$	$G_8[F_{46}]$
				2	6	
II	~20	$Fd\bar{3}m$	$G_{24}[F_{136}]$
				16	8	
III	A few	$P4_2/mnm$	$G_{30}[F_{172}]$
				10	16	4
VII	A few	$Im\bar{3}m$ or $I4/mmm$ or $Immm$	$G_1[F_6]$		Only	
Twisted	A few	$Fddd$	$G_1[F_6]$		Only	
Clathrate-like compounds showing no space tiling by clathrate-forming polyhedra:						
VIII	~10	$I\bar{4}3m$	$G_8[F_{46}]$	Strongly distorted		+ empty 8-vertex cages
IX	~20	$P4_132$	$G_{24+32}[F_{100}]$	Helical chains of

3. Clathrate Types

In the following section, the types of inorganic clathrates are described in terms of the packing of the large polyhedral cages. For all Figures, the colors of polyhedra are kept identical to those of Figure 2.1. Along with a general understanding of the crystal structure of each clathrate type, it is also important to recognize how the polyhedra are positioned with respect to each other. For this reason a simplified picture

of the relative arrangements and connectivities of polyhedra is provided for each clathrate type next to a polyhedral representation. This approach is often used for the description of complex solids [Chabot1981, Kovnir2011a].

3.1. Clathrate-I

Clathrate-I is composed of two types of polyhedra: pentagonal dodecahedra [5^{12}] and tetrakaidecahedra [$5^{12}6^2$]. These polyhedra are packed in a cubic arrangement and the space group of the majority of clathrate-I structures is $Pm\bar{3}n$. The tetrakaidecahedra share their hexagonal faces, forming columns which run along all three main crystallographic directions. The smaller pentagonal dodecahedra are not connected to each other and are surrounded only by the larger polyhedra (Figure 3.1). As indicated in Table 2.1, this clathrate type is the most realized structure type for anionic and cationic clathrates, as well as for the tetrel-free-clathrates. Specific properties and structural features of clathrate-I with respect to its superstructural ordering will be described in subsequent sections.

Figure 3.1. The crystal structure of clathrate-I: (Left) Polyhedral view showing two types of polyhedral cages pentagonal dodecahedra (blue) and tetrakaidecahedra (yellow); (Right) connectivity diagram showing how the polyhedra of each type are connected. Each polyhedron is represented as a sphere of the corresponding color. The yellow lines indicate that the tetrakaidecahedra (yellow) form linear chains by sharing hexagonal faces, while pentagonal dodecahedra (blue) are isolated from each other.

3.2. Clathrate-II

The largest clathrate-forming polyhedra, the 28-vertex, 16-faced hexakaidecahedra [$5^{12}6^4$], are present in the crystal structure of clathrate-II together with the smallest polyhedra, the pentagonal dodecahedra [5^{12}] (Figure 3.2 left). Clathrate-II crystallizes in the cubic space group $Fd\bar{3}m$. The hexakaidecahedra share all of their hexagonal faces forming a diamond-like 3D network (Figure 3.2 right). Each large polyhedron is additionally surrounded by 12 pentagonal dodecahedra, forming a truncated tetrahedron

(the light blue polyhedron in Figure 3.2 right). In this way, the complete filling of space is achieved. The unit cell of clathrate-II contains 16 small and 8 large polyhedra, with a generalized formula of $G^I_{16}G^{II}_8[F_{136}]$. Both cages can be filled with the same type of guest atoms, like Na, or with two different types of guests, like Na and Cs, with the larger cation occupying the larger cages. So far, only anionic clathrate-II structures with frameworks based on Si, Ge, and Sn atoms have been reported. It is not uncommon for clathrate-II structures to have one type of cage only partially filled, or even left completely empty. The relative ratio of the framework cage volumes to the guest cation radii determines which type of cages host the vacancies. In the Na_xSi_{136} clathrates, for compositions with small sodium contents, $x < 3$, Na preferentially occupies the large hexakaidecahedral cages, $[5^{12}6^4]$ [Beekman2010a]. In turn, for Sn-based clathrate-II structures with Ba^{2+} and K^+ guests, only pentagonal dodecahedral cages, $[5^{12}]$ are filled, and larger polyhedra are left empty [Schäfer2013].

Guest atoms can also be completely expelled from the clathrate-II cages. This is a unique property of all inorganic clathrates. The empty clathrate-II, Ge_{136} , described as new allotropic modification of germanium, was prepared by a mild oxidation of Na_4Ge_9 in ionic liquids [Guloy2006]. Additionally, an empty silicon-based clathrate-II with an extremely small residual Na content was prepared by annealing Na_xSi_{136} with iodine [Ammar2004].

Figure 3.2. The crystal structure of clathrate-II: (Left) Polyhedral view showing two types of polyhedral cages, pentagonal dodecahedra (blue) and hexakaidecahedra (orange); Right: connectivity diagram showing how polyhedra of each type are connected. Each polyhedron is represented as a sphere of the corresponding color. Hexakaidecahedra (orange) are arranged in a diamond-like tetrahedral framework by sharing all of their hexagonal faces. Each hexakaidecahedron is surrounded by 12 pentagonal dodecahedra (blue) in a truncated tetrahedral fashion.

3.3. Clathrate-III

There has been some confusion in the literature regarding the naming of the following clathrate type. In a number of publications, clathrate-IX compounds are mistakenly referred to as clathrate-III, with the most recent example found in [Fu2015]. However, this is incorrect, as a precedent was set for type III clathrates over 30 years ago, and the label actually belongs to the structural family of bromine hydrates: $(Br_2)_{20}\square_{10}[(H_2O)_{172}]$ [Jeffrey1984]. Furthermore, inorganic analogues of both cationic and anionic types were reported for the actual type III structure [Bobev2001, Zaikina2008]. Even upon first inspection, it is

obvious that the clathrate-III and clathrate-IX are drastically different structures. The former is tetragonal with 172 framework atoms, while the latter one is cubic with 100 framework atoms in the unit cell.

The crystal structure of clathrate-III is composed of three types of polyhedra (Figure 3.3). Pentagonal dodecahedra [5^{12}], tetrakaidecahedra [$5^{12}6^2$], and pentakaidecahedra [$5^{12}6^3$] are packed together in the tetragonal space group $P4_2/mnm$. The tetrakaidecahedra form two types of columns which run along the [001] crystallographic direction (Figure 3.3 right). Similar to clathrate-I, the first type of column is formed by the sharing of hexagonal faces. The second type of column, made of $5^{12}6^2$ polyhedra, is unique to clathrate-III. These are formed by pairs of tetrakaidecahedra, lying in the ab plane, which share a hexagonal face. Each polyhedral pair is fused to another pair which is rotated by 90° , by sharing 4 pentagonal faces. These chains of polyhedra run along the 4_2 screw axis (crossed dumbbells in Figure 3.3 right). The remaining space is filled by isolated pairs of either the largest pentakaidecahedra $5^{12}6^3$ or the smallest 5^{12} dodecahedra. A unit cell of clathrate-III contains 10 of the smallest, 4 of the largest, and 16 of the medium-sized polyhedra. There are 172 host framework atoms in these clathrates, and their formulas can be generalized as $G_{10}^I G_{16}^{II} G_4^{III} [F_{172}]$. Similarly to clathrate-II, the cages in clathrate-III may be filled with guests of different sizes or they may be partially vacant. The first example of an inorganic clathrate-III is $A_{30}[\text{Sn}_{172-x}\text{Na}_y\Box_z]$ ($A = \text{Cs}, \text{Cs/Rb}$) [Bobev2001]. This anionic clathrate-III exhibits a complete occupation of all of the polyhedral cages by alkali atoms and has vacancies in the tin framework. In this structure, Na plays an unusual role, partially filling up the framework vacancies.

In the cationic clathrates-III $[\text{E}_{172-x}\text{P}_x]\text{Te}_{2x}\Box_{30-2x}$, $\text{E} = \text{Si}, \text{Ge}$ [Zaikina2008, Zaikina2010, Kirsanova2013b] all of the framework sites are occupied by P and E, and all of the medium and large cages are filled with Te anions. However, the small pentagonal dodecahedra are only partially filled with Te. A similar trend was observed for the clathrate-I structures of similar elemental compositions [Zaikina2009, Kirsanova2011].

Figure 3.3. The crystal structure of clathrate-III: (Left) Polyhedral view; Right: connectivity diagram showing how polyhedra of one type are connected. Tetrakaidecahedra (yellow) form two types of channels: linear chains and dumbbell chains where each succeeding pair of polyhedra is rotated by 90° . Space in between the chains is filled with isolated pairs of either pentagonal dodecahedra (blue) or pentakaidecahedra (green).

3.4. Clathrate VII and the twisted clathrate

The ideal clathrate-VII should crystallize in the cubic space group $Im\bar{3}m$. The clathrate-forming polyhedron in this structure type is the truncated octahedron $[4^66^8]$ (Figures 2.1 and 3.4 left). In both reported crystal structures of clathrate-VII, phosphorus and transition metal atoms are segregated over separate crystallographic framework positions. This makes the square faces of the truncated octahedra non-equivalent, and it leads to a reduction of the symmetry from cubic to tetragonal, i.e. $I/4mmm$ [Johrendt1994, Keimes1995]. At temperatures below 370 K, the clathrate-VII $BaNi_2P_4$ additionally distorts down to orthorhombic, $Immm$, symmetry. The possible driving forces for this tetragonal-to-orthorhombic transition were discussed by Mewis *et al.* [Keimes1995] and Hoffmann *et al.* [Palacios1997].

Interestingly, the twisted clathrate has no analogues in gas hydrate chemistry. The two examples of twisted clathrates, $SrNi_2P_4$ and $BaCu_2P_4$ [Dünner1990, Dolyniuk2015], are based on late transition metals and phosphorus, similar to the known structures of clathrate-VII, $BaNi_2P_4$ and $BaPd_2P_4$. The crystal structure of twisted clathrate can be described as a tiling of space with unique 24-vertex polyhedra, referred to as twisted Kelvin cells (Figures 2.1a). In the twisted clathrate, M_8P_{16} polyhedra have 4 square-, 4 pentagonal-, and 6 hexagonal-faces, $[4^45^46^6]$ (Figure 2.1b and 3.4 right). According to O’Keeffe and Delgado-Friedrichs, this is one out of 10 of the possible 14-faced polyhedra which are capable of tiling space isohedrally [Delgado-Friedrichs2005].

Figure 3.4. The crystal structure of clathrate-VII (left) and that of the twisted clathrate (right). Both are formed by only one type of polyhedra which share all of their faces, completely tiling space.

3.5. Clathrate-VIII

An analogue to the clathrate-VIII structure-type has also not been found among gas hydrates. From the point of view of space tiling, it is also not a true clathrate and would be better referenced as clathrate-like, since its large polyhedral cages are not able to tile all of the space in the unit cell. Nevertheless, this clathrate type is often referred to as a clathrate and will be discussed in this chapter. One of the main reasons this type is considered a clathrate is that every clathrate-VIII is a polymorphic modification of clathrate-I, i.e. each clathrate-VIII (α -phase) upon heating transforms into a clathrate-I (β -phase) of the

same composition. The crystal structure of clathrate-VIII consists of only one type of polyhedral cage (Figure 3.5 left), which can be best described as strongly distorted pentagonal polyhedra. Such 23-vertex polyhedra can be derived from regular pentagonal dodecahedra by breaking three edges and adding three new vertices, thus forming nine new edges. Filling all of the space with such 23-vertex polyhedra is impossible, and small, vacant 8-vertex polyhedral cages are also present in the crystal structure. Eight 23-vertex polyhedra are connected to each other in such a way that their centers form a tetrahedral star, *stella quadrangula* (Figure 3.5 right). Those tetrahedral stars share all of their vertices with 8 other *stella quadrangula* polyhedra in an α -Fe type packing.

Clathrate-VIII crystallizes in the body-centered cubic space group $\bar{I}43m$, with a general formula identical to that of clathrate-I, $G_8[F_{46}]$. Only anionic clathrate-VIII structures based on Si, Ge, and Sn were reported in the literature and in every compound only one type of guest atom is present. A bonding re-arrangement on the pathway from clathrate-I to clathrate-VIII was analyzed by a topological approach based on periodic minimal surface approximants. A description of the structural transition was formulated in terms of a global transformation of the two four-connected covalent frameworks, and appears as a rotation around a distinct cubic three-fold axis [Leoni2003].

Figure 3.5. The crystal structure of clathrate-VIII: (Left) Polyhedral view; Right: connectivity diagram showing how polyhedra of one type are connected. Eight polyhedra form a tetrahedral star, *stella quadrangula*. Those tetrahedral stars share all of their vertices with another 8 polyhedra forming α -Fe-like packing.

3.6. Clathrate-IX

Similar to clathrate-VIII, clathrate-IX is also a clathrate-like structure since the chains of pentagonal polyhedra in this system are not able to tile all of the space in the unit cell (Figure 3.6). In clathrate-IX, pentagonal dodecahedra share their pentagonal faces, forming helical chains around 4_1 axes in the space

group $P4_132$. The formation of large channels in between the helical chains is clearly visible in the right part of Figure 3.6. There are 100 framework atoms in the unit cell of this clathrate, with eight guest atoms positions inside the pentagonal dodecahedra. Other open voids in the structure can host 16 to 24 cations, and a general formula can be written as $G^I_8G^{II}_x[F_{100}]$, where $16 \leq x \leq 24$. The lowest concentration of guest atoms, $x = 16$, was observed in the Si and Ge-based clathrate-IX systems, $Ba_{24}Si_{100}$ and $Ba_{24}Ge_{100}$, $G^I = G^{II} = Ba$ [Fukuoka2000a, Fukuoka2000b]. The highest concentration of guest atoms was detected for $Rb_{20}Na_{12}Sn_{100}$ ($G^I = Rb$, $G^{II} = Rb/Na$, $x = 24$) [Bobe2000a]. In clathrate-IX, part of the atoms in the framework are three-coordinated, while in all other previously discussed clathrates, all framework atoms are tetra-coordinated if no framework vacancies are present. No cationic clathrates of the clathrate-IX type have been reported.

Figure 3.6. The crystal structure of clathrate-IX: (Left) Polyhedral view; Middle: one helical chain of pentagonal dodecahedra; Right: connectivity diagram showing how the polyhedra of one type are connected. Formation of the large channels between the helical chains is clearly visible.

3.7. Clathrate-like compounds

Our knowledge of crystal structures is vast and diverse, ranging from 0-dimensional systems, such as common salts, to extended 3-dimensional cage frameworks. Consequently, many structures can be considered clathrate-like, incorporating channels, elaborate networks, and arrays of different cage types. A comprehensive summary of all clathrate-like systems is outside the scope of this review, taking into account that the term “clathrate-like” is loosely-defined. In the following, we consider many systems which have cages or clathrate fragments to be clathrate-like, and we utilize the following criteria: i) the first coordination spheres around the centroid or central atoms form large polyhedral cages with preferably 20 or more vertices; ii) the distances between the centers of the cages are much longer than the distances from the centers of the cages to the framework, and likewise they are much longer than the framework bonds. Unlike in clathrates, in clathrate-like compounds, all space in the unit cell cannot be tiled solely by polyhedral cages. The clathrates VIII and IX described above are examples of such clathrate-like compounds. Criteria (i) and (ii) allow us to discard a large number of intermetallics with small coordination numbers, as well as those consisting of channels or layers of guest atoms. For example, a very common layered structure, $ThCr_2Si_2$, at first glance seems to fit into the category of clathrates. $ThCr_2Si_2$ can be drawn as a compilation of Cr-Si cages surrounding Th atoms. Further

examination of the structure reveals that it is actually composed of layers of Si cubes encapsulating Th atoms, which are sandwiched between Cr sheets. The distances between Th atoms are equivalent to the Th-Si distances of the far vertices of the polyhedra, and the Th-Cr distances are much longer than the Th-Si distances. If the polyhedra are drawn without including the far Cr vertices, the cages are left open-ended [Ban1965]. Hence, this structure doesn't actually fit any of the criteria outlined earlier for designation as clathrate-like.

Figure 3.7. Polyhedral representations of the clathrate-like compounds separated over 4 groups with 0D, 1D, 2D, and 3D face-sharing connectivity of the clathrate-forming polyhedra. Pentagonal dodecahedra: blue, tetrakaidecahedra: yellow; other polyhedra: gray. Details and references are provided in Table 3.1.

As mentioned before, a key criterion for the description of clathrates is their long guest-guest distances, or in the case of empty cages, the long distances between the centroids of the cages. These distances are always much larger than the guest-framework distances of the guests' first coordination spheres, and furthermore, they are significantly longer than the framework-framework bonds. Structures that do not fit this description likely do not fulfill some of the other criteria, and do not fit well with the known clathrate types. The majority of clathrate-like systems possess cages or clathrate fragments, like

BaRh₂Si₉ which can be explained as layers of clathrate cages connected by “extra” framework atoms [Jung2014].

Just as a variety of clathrate structures are known, so is a comparable variety of structures containing clathrate cages and clathrate fragments. Similarly to regular clathrates, the pentagonal dodecahedron is a very common structural component for many clathrate-like structure types. This building block shows up in clathrate-like systems from 0-dimensional isolated cage structures to 3-dimensional networks of cages. In 0-dimensional BaCu₆SeTe₆, for example, the 5¹² polyhedron doesn’t share any faces, and only shares edges, leaving large voids between cages [Mayasree2011]. Likewise, BaGe₅ has isolated pentagonal dodecahedra alongside channels of Ba atoms [Aydemir2010a]. An interesting distortion in the pentagonal dodecahedra occurs in Ba₁₆Na₂₀₄Sn₃₁₀, where 5¹² becomes 5⁹1. In this case, four pentagonal dodecahedra are clustered together, one of their faces is squished and an atom is missing from each cage. This creates a nine-membered ring [Bobev2002]. Furthermore, structures composed of either 1-dimensional chains of pentagonal dodecahedra or 1-dimensional chains of tetrakaidecahedra are also known.

Some clathrate-like systems known as semiclathrates have also been studied, though they are more common among hydrates than they are among inorganic systems. Thus far, semiclathrates discovered in the realm of inorganic chemistry are limited to cationic compounds of the form [Ge_{46-x}P_x]Q_{8-y} (13.9 ≤ x ≤ 15.6; y ≤ 2.65; Q = Se, Te) and [Si₃₈Te₈]Te₈. The structures of [Ge_{46-x}P_x]Q_{8-y} are very similar to the cubic clathrate-I, but their symmetry changes from *Pm* $\bar{3}$ *n* to *Fm* $\bar{3}$ as the larger cages (tetrakaidecahedra) distort and form bonds to the guest Q atoms. These structures and their distortions from clathrate-I are discussed in a separate comprehensive review [Kirsanova2013a], and they can be related to a 2x2x2 supercell of clathrate-I. The disappearance of regular tetrakaidecahedra accompanies the generation of triply-bound framework atoms, something not seen in traditional clathrate frameworks.

While many 0-, 1-, and 2- dimensional clathrate-like frameworks are published, 3-dimensional cage frameworks seem to be the most common, though many have non-traditional polyhedra. A good example of this is NaZn₁₃ where Na atoms are at the center of 24-coordinate Zn polyhedra. Na-Na distances are long, much longer than the Na-Zn and Zn-Zn distances of the surrounding polyhedra. This structure certainly qualifies as clathrate-like, but these polyhedra do not tile together to account for all of the space in the unit cell [Ketelaar1937].

A noteworthy 3-dimensional cage framework is that of Rb₃Hg₂₀. The framework of this compound is composed entirely of Hg atoms. Interestingly, the cage structure of this amalgam looks quite similar to the traditional clathrate-I framework, forming in the same *Pm* $\bar{3}$ *n* space group and containing five unique atomic sites. However, the crystal structure of Rb₃Hg₂₀ is different from that of clathrate-I. Instead of forming the tetrakaidecahedra as in clathrate-I, different types of cages, 4⁸5⁴6² polyhedra, are present in the structure of Rb₃Hg₂₀. In turn, the pentagonal dodecahedral cages found in clathrate-I are replaced with icosahedra in Rb₃Hg₂₀. These icosahedral cages are much smaller than their pentagonal dodecahedral counterparts, and do not have enough room to accommodate Rb atoms [Todorov2000].

In short, clathrate-like can be interpreted in a variety of ways because clathrates possess such unique structures with many distinctive features. The elaborate frameworks of clathrates are not limited to one type of cage, and their cage fragments can be seen in many other structures. Simpler cages and cage-like structures are also abundant, but not many exhibit all of the same unique features of regular clathrates. Furthermore, clathrate-like structures are not limited to the Group 14 elements (Si, Ge, and Sn) that tend to be the most prominent in clathrates. They instead encompass much of the periodic table and are found to have a variety of properties.

Table 3.1. Selected examples of the clathrate-like compounds.

	Face-sharing connectivity	Cage Type	Coordination Number of Guest atom	Reference
BaCu ₆ SeTe ₆	0	5 ¹²	20	[Mayasree2011]

BaGe ₅	0	5 ¹²	20	[Aydemir2010a]
Ba ₁₆ Na ₂₀₄ Sn ₃₁₀	0	5 ⁹ 9 ¹	19	[Bobev2002]
Gd ₁₁₇ Co _{56.4} Sn _{114.3}	0	3 ⁴⁰	22	[Mudryk2013]
Te _{9.5} Si _{17.5}	0	5 ¹²	20	[Jaussaud2003]
Cs ₂ BaCu ₈ Te ₁₀	0	5 ¹²	20	[Zhang1995, Patschke2001]
Rb ₁₆ Cd ₂₅ Sb ₃₆	1	5 ¹²	20	[Zheng2010b]
Ge _{30.7} P _{15.3} Se _{5.4}	1	5 ¹²	20	[Kirsanova2013a]
Ge _{79.3} P _{29.2} S ₁₈ Te ₆	1	5 ¹² 6 ²	24	[Kirsanova2011]
Cs _{17.4} Na _{60.6} Sn ₁₃₈	2	5 ¹²	20	[Bobev2000a]
BaCu _{7.3} Sb ₅	2	3 ⁸ 6 ⁶	18	[Zheng2010a]
Ba ₃ Rh ₄ Ge ₁₆	2	4 ⁸ 6 ⁴	18	[Falmbigl2013]
BaRh ₂ Si ₉	2	4 ⁵ 5 ² 6 ⁶	22	[Jung2014]
Clathrates-VIII	3	5 ³ 6 ³ 7 ³	20	[Paschen2001]
Clathrates-IX	3	5 ¹²	20	[Carrillo-Cabrera2000]
NaZn ₁₃	3	3 ³² 4 ⁶	24	[Ketelaar1937]
KHg ₁₁	3	3 ¹⁶ 4 ⁸	20	[Biehl1999]
K ₇ Hg ₃₁	3	3 ⁶ 5 ⁶ 6 ² and 4 ⁴ 5 ⁶	18	[Todorov2000]
Rb ₃ Hg ₂₀	3	4 ⁸ 5 ⁴ 6 ²	20	[Todorov2000]

4. Trends in guest and frameworks sizes and stability of clathrates

4.1. Trends in guest and framework sizes

Clathrate frameworks are relatively flexible and are therefore able to accommodate guests of different sizes. In the following, the largest available dataset, anionic tetrel clathrates of type I, are analyzed for clathrates with Si, Ge, and Sn as the main framework elements. Figure 4.1 shows that with an increase in the average radius of the tetrel framework elements, the average framework size increases, i.e. the cubic unit cell parameter increases. For each tetrel element, the variation in framework size is dictated by the size of the cationic guest atoms.

Clathrate frameworks are often composed of more than one type of atom. Thus, a more accurate measure of the size of the clathrate framework is achieved either by using an average radius of the framework atoms or by using a unit cell parameter (Figure 4.2). The advantage of using an average radius is that only the composition is required to visualize or predict the trends. To compare unit cell parameters, they need to be determined with high accuracy, preferably by powder diffraction techniques with an internal standard. For the alkali metals A (A = K, Rb, and Cs), binary clathrates were reported for A-Si, A-Ge, and A-Sn systems. In the case of Si clathrates, the small pentagonal dodecahedra are only partially occupied by guest cations. A comparison of the top and bottom panels in Figure 4.2 shows that the basic trends are similar between the two evaluation methods. However, unit cell parameters seem to be a better option since this type of graph also reflects the changes in framework sizes for the clathrates with identical framework compositions but different guest cations. Overall, guest atoms of a particular type (Ba, K, Rb, Cs) can tolerate a range of polyhedral cage sizes, resulting in a variety of clathrate compositions for each guest atom type.

Figure 4.1. Dependence of the unit cell parameter on the type of main framework-forming element for cubic anionic clathrates-I [ICSD2015].

Figure 4.2. Dependence of (top) the average size of framework atom and (bottom) the unit cell parameter on the radius of the guest cation for cubic anionic clathrates-I [ICSD2015].

For the selected families of clathrate-I compounds with identical frameworks there is an almost linear increase of the unit cell parameters with an increase of the cation size (Figure 4.3 left). For all of the graphs with cations, the Shannon ionic radii for those cations with a coordination number of 8 were used [Shannon1976]. While those radii are not ideal measures for the cations encapsulated in the large polyhedral cages, they are still applicable to an estimation of the trends.

Similarly, a nearly linear expansion of the unit cell occurs with a variation of the tetrel elements in the clathrates where the guest atoms are identical (Figure 4.3 right). Due to the similarity of Ga and Al covalent radii, the unit cell parameters for those clathrates are very close. The size trends are important, as they allow for the prediction of changes in the unit cell parameters upon the substitution of elements in either the guest sublattice or the framework. Such substitutions are commonly used for the optimization of properties, especially in the thermoelectric applications of clathrates. Changes in the unit cell parameter are easily accessible from powder diffraction experiments and are a useful tool to estimate whether the desired substitution occurred. When larger guest cations or larger framework atoms are introduced, and a relative decrease in the clathrate unit cell parameter is observed, the formation of vacancies in either the clathrate framework or in the guest positions needs to be thoroughly considered.

Figure 4.3. Dependences of the unit cell parameters on the radius of guest cations (left) and framework atom (right) for selected families of cubic clathrate-I structures [Baran2014, Gallmeier1969, Kaltzoglou2008c, Kröner1998a, Kröner1998a, Tanaka2010, von Schnering1998, von Schnering1999, von Schnering2000, Westerhaus1977].

It should be noted that Na forms clathrates with Si-based frameworks, but no Ge- or Sn-based clathrates with Na guests have been reported. Figure 4.2 also illustrates the difficulty of incorporating trivalent rare-earth cations into clathrates. Even the largest trivalent rare-earth guest, La^{3+} , exhibits a smaller ionic radius than Na^+ , 1.16 Å vs. 1.18 Å, respectively (Figure 4.4). Thus, clathrates with trivalent rare-earth guests would require smaller frameworks, preferably with effective radii of the framework atoms equal to or smaller than those for Si. Indeed, only one example of the partial substitution of trivalent cations (La and Ce) for Ba was reported in the Au-Si framework [Prokofiev2013]. For clathrates

with K guests, there is one clathrate, $K_7B_7Si_{39}$, with a significantly smaller unit cell parameter, the point with the smallest unit cell parameter/the average size of framework atom in the K column in Figure 4.2.

Another possible way to reduce the size of the clathrate framework is to consider P-based tetrel-free clathrates. The covalent radius of P is smaller than that of Si, and when combined with transition metals, small framework sizes can be realized [Wang unpublished].

Figure 4.4. Radius (Å) of mono- and divalent metal cations in comparison with La^{3+} [Shannon1976].

4.2. Trends in the relative stabilities of clathrates

The stabilities of clathrates predominantly depend on the strengths of the covalent bonds in their frameworks, and to a lesser extent, on the types of guest atoms in their cages. Due to the high number of compounds which have been characterized, clear trends can be drawn for tetrel-based clathrates. The strength of the homoatomic E-E chemical bond decreases with increasing atomic number for $E = Si, Ge,$ and Sn . The E-E single bond energies are 226, 188, and 151 $\text{kJ}\cdot\text{mole}^{-1}$, for $E = Si, Ge,$ and Sn , respectively [Mingos1998]. Thus, the generally expected trend is that Si clathrates are more stable than Ge clathrates, which are in turn more stable than Sn-based clathrates. Substitutions or the formation of vacancies in the frameworks affect these stabilities, as do guest-framework interactions.

Decomposition or melting points determined by differential scanning calorimetry may serve as a good approximant for the stability of compounds. A comprehensive summary of the clathrates thermal stability data were reported by *Rogl et. al* [Zeiringer2012]. Data shown in figures 4.5-4.8 are taken from this work with addition of other reported data, sources of which are specified in the figure legends. In general, for the anionic clathrates based on Group 14 elements, Si clathrates have the highest melting points, the melting points for Ge-based clathrates are in an intermediate range, and Sn clathrates feature the lowest melting points (Figure 4.5). Similar trends were reported for the tetrel-free clathrates with frameworks of transition metals and phosphorus, which tend to have melting/decomposition points above 800°C, while similar clathrates with As and Sb often decompose at much lower temperatures (650°C and below) [Kovnir2011b; Dolyniuk2015; He2012; Liu2009]. Note, that there are some si-based clathrates with low thermal stability shown in lower left corner in Figure 4.5. All those compounds are un-balanced metallic phases with general composition $A_{8-x}Si_{46}$. The reason for lower stability of those phases are discussed below, see Figure 4.9 and discussion therein.

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Figure 4.6. Melting or decomposition temperatures for $\text{Ae}_8\text{Ga}_{16}\text{Ge}_{30}$ clathrates-I, Ae = Sr, Eu, and Ba [Zeiringer2012].

Figure 4.7. Melting or decomposition temperatures for $\text{Ba}_8\text{Ga}_{16}\text{E}_{30}$ clathrates, E = Si, Ge, and Sn [Deng2010, Huo2005, Kishimoto2012, Koda2014, Martin2007, Suekuni2008, Zeiringer2012].

Another example is a group of transition metal-substituted germanium and silicon frameworks with Ba guest atoms, e.g. $\text{Ba}_8\text{E}_{46-x}\text{T}_x$ (E = Si or Ge; T = Group 10, 11, or 12 transition metals or vacancies) (Figure 4.8). The overall trend in these systems remains the same, *i.e.* Si frameworks are more stable than their Ge counterparts. However, the substitution of tetrels with transition metals results in greater stabilities than the tetrel-only Ba clathrates. Overall, the melting points for the clathrates with Group 11 substituents are higher than those with Group 10 substitution. Interestingly, within the Group 10 substituents, the heavier the transition metal, the more stable the clathrate phase is for systems based on either Si or Ge. The only exception to this trend is the metastable $\text{Ba}_{7.9}\text{Ni}_{1.6}\text{Si}_{44.4}$ which was obtained by the rapid cooling of a melt between two steel plates [Aydemir2012]. The melting/decomposition temperature for this compound is almost 400°C lower than those for other $\text{Ba}_8\text{Ni}_x\text{Si}_{46-x}$ compounds. According to Rietveld refinement of the laboratory powder XRD data, $\text{Ba}_{7.9}\text{Ni}_{1.6}\text{Si}_{44.4}$ exhibited vacancies in Ba sublattice, which could be the reason for the decreased stability of this clathrate.

Figure 4.8. Melting or decomposition temperatures for $\text{Ba}_8\text{T}_x\text{E}_{46-x}$ clathrates-I, T = □, Ni, Pd, Pt; Cu, Ag, Au; Zn, Cd; $x < 8$ [Aydemir2012, Zeiringer2012].

For the Group 11 substituents, greater stability is observed for the Au clathrates. Ag clathrates have the lowest melting point within the series, and Cu clathrates are in an intermediate region. This dependence is observed for both, Ge and Si frameworks. In contrast, $\text{Ba}_8\text{Ge}_{46-x}\text{T}_x$ clathrates with $\text{T} = \text{Zn}$ are more stable than the heavier Cd-substituted clathrates. To the best of our knowledge, no stability data has been reported for the clathrates with Zn(Cd)-Si frameworks.

Within the rigid band model, electrons contributed by the electropositive guest atoms are donated to the clathrate framework. In the case of Sn-based clathrates, those extra electrons are compensated for by the formation of vacancies (see Chapter 5). Si frameworks rarely exhibit vacancies, thus the extra electrons donated by the guest atoms fill the conduction band (antibonding states), and lead to the elongation of Si-Si bonds. This, in turn, leads to reduced stability. This hypothesis can be illustrated by several examples. In the guest-deficient system $\text{Ba}_{8-x}\text{Si}_{46}$, there are no vacancies in the silicon framework, thus there are 14 excess electrons for the $x = 1$ phase. This phase is less stable than $\text{Ba}_8\text{Ge}_{43}$ with only 4 extra-electrons, because vacancy formation in the germanium framework allows for a nearly charge-balanced composition (Figure 4.8). Another example is the series of Na-Si clathrates-I and -II (Figure 4.9). The stability of those clathrates decreases with an increase in the number of extra electrons per Si framework atom, *i.e.* with increasing Na/Si ratio. Theoretically, increasing the Na/Si ratio in the clathrates with vacancy-free Si frameworks should increase the population of antibonding states, and elongate the Si-Si distances. Indeed, the Si-Si distances in the Na-deficient clathrate-II $\text{Na}_1[\text{Si}_{136}]$ lying in the range of 2.34-2.36 Å are shorter on average than the ones in the range of 2.35-2.38 Å found in Na-rich $\text{Na}_{24}[\text{Si}_{136}]$ [Beekman2010a].

The relative sizes of cations also play an important role. Small cations such as Na or Li are easily removed from a clathrate framework using chemical or physical driving forces, such as iodine or HCl reagents, or using an applied voltage potential, a vacuum or temperature change. Larger ions such as K^+ or Ba^{2+} cannot diffuse from the clathrate cages without destroying the frameworks. This is reflected in the higher stabilities of $\text{K}_7[\text{Si}_{46}]$ and the mixed-guest $\text{Na}_2\text{Ba}_6[\text{Si}_{46}]$ clathrates. It should be noted that, in these systems, the rigid band model and the assumption of a complete charge transfer are not the only factors affecting the stabilities of these clathrates. Moreover, theoretical calculations for $\text{Ba}_{8-x}[\text{Si}_{46}]$ indicate that $\text{Ba}5d$ states are strongly hybridized with the valence states of the Si framework, providing an additional stabilization effect [Moriguchi2000a, Saito1995, Connetable2003].

Figure 4.9. Decomposition temperatures for Na-Si, K-Si, and Na-Ba-Si clathrate-I systems. [Beekman2006, Böhme2007a, Böhme2007b, Horie2009].

5. Charge balance and Zintl count

The Zintl concept is a powerful tool that allows for the prediction of electronic properties and for a rationalization of the structures of many polar intermetallic compounds, including clathrates [Kauzlarich1996, Miller2011]. The Zintl concept postulates two simple principles: (1) a full charge transfer takes place between anionic and cationic sublattices, and (2) an electron octet is realized by each atom. For cationic/anionic guests, this means they will donate/accept electrons to/from the framework to stay in a closed-shell, noble gas configuration, like K^+ or Br^- (Figure 5.1). Clathrate framework atoms are all four-coordinated, with only one exception, clathrate-IX, where three-coordinated framework positions are intrinsically present. In all other clathrates, three-coordinated framework sites can be generated by the formation of framework vacancies. Tetra-coordinated framework atoms need four electrons to form four covalent bonds, while three-coordinated framework atoms need five electrons to form three covalent bonds plus an electron lone pair pointed towards the vacancy (Figure 5.1). This describes the total electron count for clathrate frameworks. If the total number of available valence electrons is exactly sufficient to satisfy all bonding requirements in the clathrate, semiconducting properties are expected (Figure 5.1, bottom middle). The bandgaps for semiconducting clathrates are typically below 2 eV. For otherwise similar clathrate compositions, the bandgaps of tetrel clathrates decrease from Si- to Ge- to Sn-based ones. Clathrate compositions with extra electrons exhibit metallic-like properties with electrons as the dominant charge carriers, while a lack of electrons leads to metallic-like properties with holes as the main charge carriers (Figure 5.1 bottom left and right).

Figure 5.1. A scheme summarizing the basic principles of Zintl electron counting for clathrates. Triply-bound and tetra-coordinated atoms in the fragments of the clathrate framework are drawn in yellow and black, respectively.

Let us consider a few examples of clathrate compositions to illustrate clathrate electron counting (Table 5.1).

Ba₈[Ga₁₆Ge₃₀]: Each Ba atom donates 2 electrons to the framework, becoming Ba^{2+} . No vacancies are present in the framework, thus 4 electrons are required per framework atom to achieve an electron-balance. Since there are 46 atoms in the framework, a total of $46 \times 4 = 184$ electrons are required. The number of electrons available is $8 \times 2 = 16$ (Ba) plus $16 \times 3 = 48$ (Ga) plus $30 \times 4 = 120$ (Ge), for a total of 184

electrons. Thus, the compound is electron-balanced and it is expected to exhibit semiconducting properties.

K₈[Sn₄₄□₂]: This clathrate has two framework vacancies, each surrounded by four Sn atoms. Thus, the total number of 3-coordinated Sn atoms (3b-Sn) is 8, and the total number of 4-coordinated Sn atoms (4b-Sn) is 36. As mentioned earlier, 3-coordinated framework atoms require 5 electrons. The total number of electrons necessary for the framework is therefore $8 \times 5 = 40$ (3b-Sn) plus $36 \times 4 = 144$ (4b-Sn), and the total number of electrons required is 184. The total number of valence electrons available is $8 \times 1 = 8$ (K) and $44 \times 4 = 176$ (Sn), for a total of 184 electrons. The compound is electron-balanced and it is expected to exhibit semiconducting properties.

Ba₈[Ge₄₃□₃]: This clathrate has three framework vacancies, each surrounded by four Ge atoms. Thus, the total number of 3-coordinated Ge atoms (3b-Ge) is 12, and the total number of 4-coordinated Ge atoms (4b-Ge) is 31. We assume there is no clustering of vacancies, which is a reasonable assumption for such a small concentration of vacancies. The total number of electrons required for the framework is therefore $12 \times 5 = 60$ (3b-Ge) plus $31 \times 4 = 124$ (4b-Ge), and the total number of electrons required is 184. The total number of valence electrons available is $8 \times 2 = 16$ (Ba) and $43 \times 4 = 172$ (Ge), for a total of 188 electrons. Hence, this compound is not electron-balanced and it is expected to exhibit metallic-like properties with electrons as the main charge carriers.

Ba₈[Cu₁₆P₃₀]: This clathrate has no framework vacancies, each Cu and P atom is tetrahedrally coordinated. The total number of electrons required for the framework is therefore $46 \times 4 = 184$. To calculate the number of electrons available, we assume that Cu has stable d^{10} electron configuration and provides only one s -electron for bonding. The total number of valence electrons available is $8 \times 2 = 16$ (Ba), $16 \times 1 = 16$ (Cu), and $30 \times 5 = 150$ (P), for a total of 182 electrons. Hence, this compound is not electron-balanced and it is expected to exhibit metallic-like properties with holes as the main charge carriers. Characterization of the transport properties confirmed the metallic-like resistivity and small positive values of Seebeck thermopower typical for p -type materials.

[Ge₃₈P₈]₈: Each iodine atom requires 1 electron to complete its electron octet and reach an I^{-} configuration. No vacancies are present in the framework. Therefore $46 \times 4 = 184$ electrons are necessary for this framework to be charge-balanced and the total number of required electrons is $184 + 8 = 192$. The total number of electrons available is $8 \times 5 = 40$ (P) plus $38 \times 4 = 152$ (Ge), for a total of 192 electrons. Thus, the compound is electron-balanced and it is expected to exhibit semiconducting properties.

[Sn₂₄P_{19.2}□_{2.8}]₈Br₈: Since this clathrate has 2.8 vacancies in the framework, the number of 3-coordinated framework atoms is $4 \times 2.8 = 11.2$. The number of electrons required: $8 \times 1 = 8$ (Br) plus $11.2 \times 5 = 56$ (3b-Sn/P) plus $32 \times 4 = 128$ (4b-Sn/P), for a total of 192 required electrons. The number of valence electrons available is $24 \times 4 = 96$ (Sn) plus $19.2 \times 5 = 96$ (P), or 192 total electrons. The compound is electron-balanced and it is expected to exhibit semiconducting properties.

[Sn₂₀Zn₄P_{20.8}□_{1.2}]₈: This clathrate has 1.2 vacancies in the framework, so the number of 3-coordinated framework atoms is $4 \times 1.2 = 4.8$. The total number of electrons required is $8 \times 1 = 8$ (I) plus $4.8 \times 5 = 24$ (3b-Sn/Zn/P) plus $40 \times 4 = 160$ (4b-Sn/Zn/P), for a required total of 192 electrons. The number of valence electrons available is $20 \times 4 = 80$ (Sn) plus $4 \times 2 = 8$ (Zn) plus $20.8 \times 5 = 104$ (P), or 192 total. This compound is electron-balanced and it is expected to exhibit semiconducting properties.

Those examples illustrate that the determination of whether a clathrate phase is electron-balanced or not can be achieved regardless of the number of different types of elements making up a framework, and regardless of the number of vacancies present in either the framework or guest positions. The only factors which need to be correctly determined are the total number of valence electrons available, and the

required number of valence electrons, taking into account the number of 4- and 3-coordinated framework atoms. With this knowledge in hand, the semiconducting composition of any clathrate can be predicted. Thus, the Zintl concept has strong predictive power which allows for the formulation of semiconducting compositions prior to their synthesis. For example, $K_8[Si_{46}]$ has 192 valence electron but only 184 are required for proper four-coordinate bonding in the framework. These extra electrons are situated in the conduction band, occupying antibonding states, reducing the overall stability of this compound compared to other electron-balanced Si clathrate-I systems. To compensate for the extra electrons of K, framework substitution is required. The substitution of Si with an element with fewer valence electrons, *i.e.* $K_8[Al_8Si_{38}]$, generates an electron-balanced system, since the total number of valence electrons is now 184 [Sui2015].

Another example is a clathrate-III phase in the Si-P-Te system. The composition of this phase can be written as $[Si_{172-x}P_x]Te_{30-y}\square_y$ [Zaikina2008]. Using a Zintl formalism we can not only determine the relationship between x and y , but we can also determine which compositions should be electron-balanced. There are no vacancies in the framework and all framework atoms are 4-coordinated, leading to $172 \times 4 = 688$ required electrons. Each Si atom supplies 4 electrons and each P provides 5 electrons, in this way the total number of electrons available is $688+x$. Each Te guest anion requires 2 electrons to become Te^{2-} , thus the total number of electrons required is $60-2y$. To balance the excess electrons over 688, x should be equal to $60-2y$. Indeed, the experimentally-determined composition $[Si_{130}P_{42}]Te_{21.2(1)}\square_{8.8}$ with $x = 42$ and $y = 8.8$ is close to the expected electron-balanced composition of $x = 42$ and $y = 9$ [Zaikina2008, Zaikina2010].

Table 5.1. A summary of electron counting for clathrates. FU is the formula unit and VEC is the valence electron count.

Ba₈[Ga₁₆Ge₃₀]							
Available				Required			
	Number per FU	VEC	Electrons available		Number per FU	VEC required	Electrons required
Ba	8	2	16	4b-Ga	16	4	64
Ga	16	3	48	4b-Ge	30	4	120
Ge	30	4	120				
Total			184	Total			184
K₈[Sn₄₄□₂]							
Available				Required			
	Number per FU	VEC	Electrons available		Number per FU	VEC required	Electrons required
K	8	1	8	3b-Sn	8	5	40
Sn	44	4	176	4b-Sn	36	4	144
Total			184	Total			184
Ba₈[Ge₄₃□₃]							
Available				Required			
	Number per FU	VEC	Electrons available		Number per FU	VEC required	Electrons required
Ba	8	2	16	3b-Ge	12	5	60
Ge	43	4	172	4b-Ge	31	4	124
Total			188	Total			184

Ba₈[Cu₁₆P₃₀]							
Available				Required			
	Number per FU	VEC	Electrons available		Number per FU	VEC required	Electrons required
Ba	8	2	16				
Cu	16	1	16	4b-Cu	16	4	64
P	30	5	150	4b-P	30	4	120
Total			182	Total			184
[Ge₃₈P₈]I₈							
Available				Required			
	Number per FU	VEC	Electrons available		Number per FU	VEC required	Electrons required
Ge	38	4	152	4b-Ge	38	4	152
P	8	5	40	4b-P	8	4	32
				I	8	1	8
Total			192	Total			192
[Sn₂₄P_{19.2}□_{2.8}]Br₈							
Available				Required			
	Number per FU	VEC	Electrons available		Number per FU	VEC required	Electrons required
Sn	24	4	96	4b-Sn	12.8	4	51.2
P	19.2	5	96	3b-Sn	11.2	5	56
				4b-P	19.2	4	76.8
				I	8	1	8
Total			192	Total			192
[Sn₂₀Zn₄P_{20.8}□_{1.2}]I₈							
Available				Required			
	Number per FU	VEC	Electrons available		Number per FU	VEC required	Electrons required
Sn	20	4	80	4b-Sn	15.2	4	60.8
Zn	4	2	8	3b-Sn	4.8	5	24
P	20.8	5	104	4b-Zn	4	4	16
				4b-P	20.8	4	83.2
				I	8	1	8
Total			192	Total			192

6. Synthesis of clathrates

Inorganic clathrates exhibit fascinating structural chemistries and may find use in various applications such as thermoelectrics, superconductors, and Li-ion batteries. Prior to discussing the applications of inorganic clathrates, we will consider how to synthesize them. Various synthetic methods will be mentioned in the following chapter, but are also summarized in several reviews and book chapters [Nolas2014; Shevelkov2011]. Here, we divide the synthesis methods into three main categories based on the size of crystals these methods often produce: microscopic synthesis, mesoscopic synthesis, and finally macroscopic synthesis. The microscopic synthesis methods produce samples with crystallite sizes of less than 10 micrometers, often obtained as homogenous powder. Methods such as thermal decomposition, conventional solid state synthesis, and soft chemistry can be classified under microscopic synthesis methods. Intermediate sizes are produced by mesoscopic synthesis methods, which usually produce crystallites with sizes between a millimeter and a micrometer. These methods include flux syntheses and spark plasma sintering (SPS). Macroscopic syntheses are methods that yield large crystals, often larger than a millimeter. These include the Czochralski method, vertical Bridgman growth, and floating zone growth. Though we break these methods into three categories, the sizes of samples achievable by the methods discussed actually overlap significantly. Thus, our categories are merely a general description for the various synthetic methods. Occasionally, microscopic and mesoscopic syntheses can form millimeter-sized crystals. A schematic for the classification of clathrate synthesis methods is shown in Figure 6.1.

Figure 6.1. A schematic showing classification of different synthetic methods with respect to the crystallite sizes they yield. The orange and blue lines indicate the arbitrary 10 micrometer and 1 millimeter boundaries we use for this classification. Microscopic synthesis methods are on the left of the orange line, mesoscopic synthesis methods are in the middle, and macroscopic synthesis methods are to

the right of the blue line. Photo above: samples with different crystallite sizes synthesized in Kovnir group at UC Davis.

6.1. Microscopic synthesis

6.1.1. Thermal decomposition

Half a century ago, thermal decomposition was the first method used to synthesize an inorganic clathrate and it is still used today as a viable synthetic method [Schäfer1961, Witte1964]. In this method, the binary compounds, A_xE_y (A = alkali metal, E = Si, Ge, $x \approx y$), are pre-synthesized and used as precursors. When heated under vacuum or inert atmosphere, clathrate samples are generated by a depletion of the alkali metals from A_xE_y phases. The temperature and atmosphere (either vacuum or the pressure of alkali metals) play critical roles in the decomposition process [Kasper1965; Cros1970a; Cros1970b; Ramachandran2000; Latturmer2001]. One commonly used precursor is AE [A = Na, K, Rb, E = Si, Ge], which can be decomposed to generate either clathrate-I or clathrate-II systems depending on the conditions. For instance, in the Na-Si system, binary NaSi compound begins to decompose at 633 K, but the formation of clathrate-I Na_8Si_{46} only occurs at much higher temperatures in the presence of sodium metal vapor. Additionally, further increasing the reaction temperature can actually hamper the formation of clathrate-I Na_8Si_{46} due to its instability over 793 K. In the synthesis of clathrate-II Na_xSi_{136} , temperatures below 713 K are favorable when the presence of sodium metal vapor is minimized [Horie2009]. Furthermore, investigations into the decomposition of NaSi demonstrated Na pressure has a considerable impact on the identity of the final clathrate products of these thermal decomposition reactions [Cros1970a; Cros1970b; Ramachandran1999].

Thermal decomposition is widely used to produce Si-based clathrates in the form of very fine powders with crystallite sizes in the submicron to micron range [Baitinger2007]. Rapid thermal decomposition introduces substantial crystal defects, including: stacking faults, twin interfaces, and possible surface oxidations, hampering our understanding of the intrinsic physical properties of these binary clathrates [Nistor1994, He2001]. Another limitation of the thermal decomposition process is the difficulty of purification, as a mixture of the target phase is often present along with other clathrate types [Cros1970a; Cros1970b; Ramachandran1999]. The thermal decomposition process was recently modified by *Toberer et al.* who introduced a water-cooled copper cold-plate on top of the crucible containing the NaSi precursor. This setup allowed them to maintain a low Na vapor pressure during NaSi decomposition, which in turn resulted in the phase-selective synthesis of type II silicon clathrates [Krishna2014].

Though many questions about the thermodynamics and kinetics of thermal decomposition remain unanswered, this method is still very useful for the identification and synthesis of many new clathrate phases [Hutchins2011, Liang2015]. It has been especially helpful in the formation of “guest-free” silicon frameworks, which may inspire new research interest and potential applications [Ammar2004].

6.1.2. Solid state synthesis

Solid state synthesis (i.e. the reaction of components at elevated temperatures) is a widely-used method for the production of a broad range of clathrate phases. The outcome of such solid state reactions depends on a number of variables which can be varied to yield different products. Such variables can include: the identity of starting materials and their vapor pressures or reactivities, the heating and cooling profiles of the reaction, the crucible type and volume, *etc.* Pure elements are often chosen as reaction materials. In these cases, the reactivities and melting/sublimation temperatures of the elements greatly affect the reaction process. Most clathrate frameworks are built up of the Group 14 elements Si, Ge, and Sn. The high melting point (1687 K) and low reactivity of elemental Si means that high temperatures are often required for the direct synthesis of Si-based clathrates from elements [Fukuoka2004]. On the other hand, the Sn-based clathrates can be synthesized at much lower temperatures since Sn melts at 505 K

[Kaltzoglou2007; Dubois2005; Kaltzoglou2008a, Kaltzoglou2008b, Kaltzoglou2008c, Kaltzoglou2009, Shatruck1999, Kovnir2004c, Zaikina2007a, Zaikina2007b]. In some cases, pre-reacted binary precursors produced from the heating or arc-melting of elements can be used. In this way, the limitations of using elemental precursors can be overcome, averting potential issues with high vapor pressures or the chemical inertness of elements. For example, the $\text{Sr}_8\text{Ga}_x\text{Si}_{46-x}$ clathrate was synthesized in two stages: arc-melting of the elements was used to prepare a polycrystalline multiphase sample, which was further processed and purified via the float zone melt method mentioned later in this chapter [Imai2002]. Other examples are the clathrates-I $\text{A}_8\text{Hg}_{3+x}\text{Ge}_{43-x}$ ($\text{A} = \text{K}, \text{Rb}$) which were prepared from A_4Ge_9 and Hg or HgO starting materials [Kaltzoglou2008b]. $\text{K}_7\text{B}_7\text{Si}_{39}$ was also made by a similar two-step method, in which boron and silicon were arc-melted first to form a precursor, which was further reacted with an excess of potassium to yield the $\text{K}_7\text{B}_7\text{Si}_{39}$ clathrate. The potassium residue was washed out after the reaction had reached completion [Jung2007]. Due to the varied thermal properties and reactivities of the clathrate-forming elements and of the target clathrate phases, a very wide temperature range is used for solid state synthesis. $\text{Cs}_8\text{M}_{18}\text{Sb}_{28}$ ($\text{M}=\text{Zn}, \text{Cd}$) can be obtained at 823 K [Liu2009], while the formation of $\text{Ba}_{8-x}\text{Si}_{46}$ requires the higher temperature of 1573 K with the additional application of high pressures [Fukuoka2004]. Such temperatures are often achieved in resistance or induction furnaces.

The proper choice of crucible material is crucial for the success of a solid state reaction. Using a suitable crucible prevents side-reactions of the crucible with the reactants, thus minimizing the costs associated with having to constantly purchase new crucibles. More importantly, it also prevents contamination of the target clathrate phase with components of the crucible materials. With that being said, crucibles constructed of glassy carbon (both stand-alone crucibles and thin coatings on the inside of silica tubes), alumina, niobium, tantalum, and boron nitride (BN) have been used in the syntheses of clathrate phases. In the solid state synthesis process, multiple cycles of annealing and homogenizing through grinding can be helpful in obtaining pure phases. In the synthesis of BaCu_2P_4 , a tetrel-free phosphorus-based clathrate, the sample was ground and annealed three times at a temperature below the decomposition point to avoid the formation of another clathrate phase with a similar composition, $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$ ($\text{BaCu}_2\text{P}_{3.75}$), which is stable at higher temperatures [Dolyniuk2015]. Solid state synthesis is a widely-available method that can be useful in producing new phases. This method often produces uniform polycrystalline powders with crystallite sizes in the range of 0.1-100 μm , though occasionally larger-sized single crystals over 1 millimeter can be grown by this method [Wang unpublished].

6.1.3. Soft chemical synthesis

The soft chemical method we refer to here involves the redox reactions of certain pre-synthesized solid precursors, generally taking place under gaseous HCl or in ionic liquids [Nolas2014]. This method is useful for the stabilization of many metastable phases and new products since it does not require the high temperatures needed for many other synthesis methods [Nolas2014; Guloy2006; Böhme2007a; Böhme2007b]. An example of the applicability of this method is to the new, metastable elemental allotrope of germanium, Ge_{136} , a guest-free clathrate-II. This Ge allotrope was synthesized in the ionic liquid: dodecyl trimethyl ammonium chloride and aluminum trichloride (DTAC/ AlCl_3) at 573 K [Guloy2006]. This modification has not been accessible through other synthetic methods. Since soft chemical reactions are carried out at much lower temperatures, $T < 700$ K, clathrates containing guest cations, such as clathrate-II $\text{K}_{8.6}\text{Ge}_{136}$, can also be produced by this method [Guloy2009]. Another frequently used oxidizer, gaseous HCl, was also successfully applied for the production of clathrate phases. In this case, HCl was generated in-situ by the thermal decomposition of solid NH_4Cl . The precursors used in this method were similar to those of the thermal decomposition reactions mentioned earlier, and the side products were often water soluble. The clathrates $\text{Na}_2\text{Ba}_6\text{Si}_{46}$ [Böhme2007b], $\text{Na}_8\text{Si}_{46}$, $\text{K}_{8-x}\text{Si}_{46}$ [Böhme2007a], and $\text{Ba}_{8-x}\text{Si}_{46}$ [Liang2011] have all been obtained by this method. Another interesting example of a soft oxidation reaction is the reaction of WO_3/HgO with the Zintl phase K_4Ge_9 to produce the clathrate-I $\text{K}_4\text{Hg}_{3+x}\text{Ge}_{43-x}$ [Kaltzoglou2008b]. This example illustrates the highly underexplored potential of soft chemistry routes to the synthesis of inorganic clathrates.

6.2. Mesoscopic synthesis

6.2.1. Flux growth

The flux method is a very common and useful tool for the discovery of inorganic materials [Kanatzidis2005, Canfield1992]. With this method, raw materials (elements) are dissolved in a flux, *a.k.a.* a high temperature solvent. Choosing a suitable flux is crucial for this type of reaction, as the properties of the flux and the flux-solute interactions need to be taken into account. Various types of fluxes ranging from salts to molten metals are used to synthesize the clathrate phases. Salt fluxes are often desirable for many reactions because they are easily removed by water or other solvents. As an example, during the investigation of the Ni-based tetrel-free clathrates BaNi_2P_4 and SrNi_2P_4 , a BaBr_2 flux was proven to be suitable for growth of the target phase, ultimately increasing the reactivity of elements and reducing the reaction time [Dolyniuk2015]. Elemental metals are another commonly used flux in the synthesis of inorganic clathrates. As previously noted, the high melting points of Si (1687 K) and Ge (1211 K) usually require high temperature for the direct reactions of elements, but fluxes can be used to lower reaction temperatures. Many metal fluxes with lower melting points such as gallium, indium, zinc, tin, bismuth, lead, sodium, *etc.* can be used to obtain clathrate phases at lower temperatures. For example, aluminum was demonstrated to be a good reactive medium in the Ba-Al-Si system. In this system, the reaction can take place at 1273 K, significantly below the melting point of Si (1687 K) [Condrón 2005; Condrón2006a; Condrón2008]. Another advantage of the metal flux method is the growth of sizable (often up to 1 cm) high-quality single crystals, which are useful for the investigation of the intrinsic physical properties of a compound. For instance, huge single crystals of up to 1 cm of clathrate-I and clathrate-VIII $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$ were obtained via a self-flux method using an excess of Ga or Sn at 763 K [Suekuni2008]. Large single crystals of clathrate-I phases in the Ba-Ga-Ge system, up to 60 mg, were also synthesized via gallium excess which was used as a flux [Lattner2002]. In some cases, the combinations of salt and metal fluxes have also been successfully used to grow clathrate crystals. In the case of $\text{A}_8\text{Al}_8\text{Si}_{38}$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$), a mixed flux composed of Al and the respective alkali-metal halide salt (KBr or RbCl or CsCl) was used to produce high quantities of large single crystals [Baran2014].

6.2.2. SPS synthesis

SPS (spark plasma sintering) is an effective consolidation method, used to sinter a wide range of technologically-important materials, mainly ceramics and nanostructured materials. The SPS method combines both high pressure (with maximum pressures below 1 GPa) and high temperature ($T > 1300 \text{ K}$) under vacuum or inert atmosphere. Heat is generated in the sample by passing a current through the pressure die, *i.e.* through the sample itself. Aside from the consolidation of powder samples, SPS methods were recently demonstrated to be a powerful tool for crystal growth [Omori2000]. The presence of high temperature and pressure has been shown to aid in the synthesis of many inorganic clathrate phases [Beekman2009; Hayashi2010; Stefanoski2013, Dong2015]. For instance, the vacancy-free $\text{Na}_8\text{Si}_{46}$ and $\text{Na}_{24}\text{Si}_{136}$ clathrate-I and clathrate-II systems can be obtained via the SPS method [Beekman2009]. In these syntheses, the temperature profiles and applied pressures play critical roles in the outcome of the SPS experiment. $\text{Na}_{24}\text{Si}_{136}$, for example, was prepared by pressing the NaSi starting material at 823–973 K and 100 MPa for three hours [Beekman2009]. The SPS process has also been useful in more complex clathrate systems such as the five-element system $\text{Ba}_6\text{A}_2\text{AuGa}_x\text{Si}_{45-x}$ ($\text{A} = \text{Sr}, \text{Eu}; x = 13, 14$) [Koga2009]. Many inverse clathrate phases can also be synthesized by SPS methods, including clathrate-I phases in the Si–P–Te, Ge–P–Te, and Sn(Ge)–Sb–I systems [Kishimoto2006a; Kishimoto2006b; Kishimoto2007].

6.3. Macroscopic synthesis

From an applications point of view, it is hard to determine whether a polycrystalline sample or a single crystal is better suited overall; the answer will depend on the application. For the purpose of investigating

the intrinsic properties of solids, single crystals are undoubtedly superior to polycrystalline samples due to the absence of grain boundaries. In the same vein, the highest thermoelectric efficiency for clathrates was reported in a single crystal grown via the Czochralski method [Saramat2006]. Recently, large single crystals of clathrates have been considered attractive alternatives to polycrystalline sintered pellets because they allow for the measurements of intrinsic properties while avoiding the effects of grain boundaries [Nolas2014]. Below, three frequently used methods are discussed which can produce sizeable single crystals (> 1 cm) of clathrates.

6.3.1. Czochralski methods

The Czochralski process involves the growth of large single crystals by the slow pulling of a seed crystal out of the melt. This method has played a critical role in modern technologies, particularly in the growth of silicon semiconductors for their use in integrated circuits. The Czochralski process is greatly affected by the temperature gradient, pulling rate, seed crystals' habits, crucible materials, and by the reaction atmosphere. The high reported ZT value, 1.35 at 900 K (n -type), was found in a disk sample cut from a Czochralski-grown single crystal of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ [Saramat2006]. Interestingly, another Czochralski-grown single crystal of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ was reported a few years later to have ZT of 0.8 at 1050 K [Toberer2008]. In this system, the Ga/Ge ratio is highly tunable, leading to a possible elemental distribution gradient in the single crystal. This in turn may be the cause of this large discrepancy in the measured properties of two separate single crystals produced by the same method. Additionally, a careful investigation of the growth process of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ demonstrated that the Ga/Ge ratio, and correspondingly, the physical properties of a single crystal are affected by such parameters as the pulling rate and the pressure of the reaction chamber [Hou2009]. Likewise, a quaternary compound with the nominal stoichiometry of $\text{Ba}_8\text{Ga}_{16}(\text{Si}_{0.25}\text{Ge}_{0.75})_{30}$ was grown via the Czochralski method. This clathrate exhibits a continuous range of stoichiometries, ranging from $x = 0.2$ in $\text{Ba}_8\text{Ga}_{16}(\text{Si}_x\text{Ge}_{1-x})_{30}$ up to $x = 0.41$ along the pulling direction [Christensen2009]. The Czochralski method has also been applied in the synthesis of Si-based clathrates, $\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$ [Nagatomo2012; Mugita2011] and the Ga-doped clathrate $\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$ [Onizuka2014]. Crystals of clathrate types other than clathrate-I were also grown by the Czochralski method, including large crystals of the clathrate-IX $\text{Ba}_{24}\text{Ge}_{100}$ [Fukuoka2000a].

6.3.2. Floating zone growth

Floating zone growth was developed over half a century ago. This is a rapid crystallization method, which makes it more kinetically-driven than other methods. Impressively, this method has recently allowed for the incorporation of rare earth elements into the $\text{Ba}_8\text{Au}_x\text{Si}_{46-x}$ clathrate. The rare-earth-doped samples have shown a 50% enhancement of their power factors compared to those of the undoped parent samples [Prokofiev2013]. In these experiments, this powerful growth method allowed for overcoming the difficulties of introducing the small rare earth elements into clathrate polyhedral cages. Additionally, the elemental distribution [Prokofiev2014] and the mechanism of rare earth incorporation [Prokofiev2016] in $\text{Ba}_8\text{Au}_x\text{Si}_{46-x}$ were carefully investigated, and it was determined that the overall driving force for rare earth atoms' incorporation in this clathrate was a combination of the charge balance and the amount of free space inside the cages. Other examples, such as $\text{Sr}_8\text{Ga}_x\text{Si}_{46-x}$ [Imai2002] and $\text{Ba}_8\text{Cu}_{4.8+y}\text{Ga}_x\text{Ge}_{41.2-x-y}$ [Prokofiev2014] have also been synthesized by the floating zone growth method. Interestingly, the presence of transition metals and rare earth elements in the clathrate may open a new window for the magnetic applications of clathrates. The floating zone method is also useful in the discovery of many other cage compounds, which are hard to obtain from other methods, such as $\text{RB}_{44}\text{Si}_2$ ($\text{R}=\text{Y}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$) [Hossain2016]. The main drawback for this method is the high cost of the instrument.

6.3.3. Vertical Bridgman growth

The vertical Bridgman growth process is another crystallization method in which single crystals are grown directly from the melt. Usually, raw materials are put into crucibles made of a variety of materials, including graphite, glassy carbon, silicon, BN, and metals, and these crucibles are sealed inside silica tubes. In the ideal case, all reagents melt congruently, forming a uniform melt with limited evaporation. Several fundamental complications can reduce the performance of this method, including: high melting points of reactants and high vapor pressures of the melts at elevated temperatures. Some practical considerations for this method include the necessity of using a vertical furnace and the requirements of specialized crucibles. In the clathrate family, mainly Ge- and Sn-based compounds are synthesized using this method. Good quality single crystals of $\text{Ba}_8\text{Ni}_{3.5}\text{Ge}_{42.1}\square_{0.4}$ were grown in a glassy carbon crucible in the high temperature zone of 1273 K [Nguyen2010]. Similarly, $\text{Ba}_8\text{Au}_{5.3}\text{Ge}_{40.7}$ was first pre-annealed in a glassy carbon crucible at 1398 K for 12 hours in the upper zone and then slowly removed from this temperature zone [Zhang2011]. The thermoelectric efficiency of the $\text{Ba}_8\text{Au}_{5.3}\text{Ge}_{40.7}$ single crystals grown by this method reached a promising ZT value of 0.9 at 680 K. The Sn-containing clathrates can be grown from much lower temperatures, such as in the case of p -type $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$ and n -type $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$, which were obtained at 833 K and 723 K, respectively. Additionally, this example demonstrates the ability of the Bridgman method to meet the demands of tuning both the charge carrier concentration and the type of carriers [Chen2014]. Vertical Bridgman growth can also lead to polycrystalline clathrate samples of $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$ grown from a $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$ melt [Hong2014]. We have also recently demonstrated that the vertical Bridgman method can be applied to the phosphorus-based clathrates, despite concerns of the high vapor pressure of phosphorus in the melt [Wang unpublished].

6.4. Other routes

Aside from the aforementioned methods, there are still several other useful synthetic routes which can be applied to clathrate research.

6.4.1. High pressure synthesis

Earlier we mentioned the SPS methods, in which both high temperature and pressure are present. In the SPS methods, pressure is limited to 1 GPa. Alternatively, the high pressure method mentioned here refers to synthesis pressures of over 1 GPa. Syntheses at such an extreme pressures offer new insight into the structures and properties of solids, which cannot be accessed under ambient pressures. The high pressure method is also very important for clathrate research, as demonstrated by the discovery of the bulk clathrate superconductor $\text{Ba}_{8-x}\text{Si}_{46}$ [Yamanaka2000]. The cationic content of $\text{Ba}_{8-x}\text{Si}_{46}$ was found to be tunable, leading to large effects on the superconducting critical temperatures as it will be discussed in **Chapter 8.3**. Other Si clathrates, such as $\text{Cs}_{8-x}\text{Si}_{46}$, were also synthesized by a high pressure technique [Wosylus2009]. This method can also be applied to the inverse clathrate system Si-Te, in which two polymorphs of $[\text{Si}_{38}\text{Te}_8]\text{Te}_8$ can be generated by high pressure synthesis [Jaussaud2004]. Lastly, clathrate-I $[\text{Ge}_{43.3}\text{I}_{2.7}]\text{I}_8$, was synthesized using high pressures achieved not by a high pressure apparatus, but *via* pressurizing an inert gas, such as Xe and CO_2 . The high pressures of these inert gases influence the thermal decomposition of GeI_2 leading to the clathrate-I $[\text{Ge}_{43.3}\text{I}_{2.7}]\text{I}_8$ [Nesper1986].

6.4.2. Transport synthesis

Transport agents are usually used in the formation of cationic clathrates, where the guest atoms are halogen or chalcogen anions. The selection of a volatile transport agent is determined by the physical and chemical properties of the particular system. Elemental iodine can act as a transport agent and reactant in the preparation of $\text{Si}_{40}\text{P}_6\text{I}_{6.5}$ [Kovnir2004a]. More frequently, the binary halides, such as SnI_4 , TeI_4 , TeCl_4 , HgBr_2 , and Hg_2Cl_2 , are used as transport agents in the formation processes of cationic clathrates [Shatruck2001; Kovnir2004c; Kovnir2006; Philipp2008].

In summary, we have discussed several methods used for the synthesis of polycrystalline and single crystalline samples of inorganic clathrates. Recently, several examples of the micro- and nano-structuring of clathrates in the form of thin films and isolated nanoparticles have also been reported. An example is the clathrate $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$, which was grown as a thin film on a variety of substrates [Witanachchi2006]. Methods such as ball milling and sol-gel synthesis, as well as melt-spinning have been used to generate micro- and nano-structured clathrates [Shirataki2011; Pacheco2016; Christian2015]. Assuming that the current interest in clathrate phases persists, the list of known clathrates and their methods of synthesis will certainly increase.

7. Structures and compositions of clathrates

7.1. Challenges and pitfalls in compositional and structural determinations

Clathrates crystallize in highly symmetrical crystal structures with only a few crystallographic positions in their frameworks. Clathrate-I for example, contains only three framework positions in the $Pm\bar{3}n$ space group: $24k$, $16i$, and $6c$. Many ternary and quaternary clathrates-I were reported, and examples showing the presence of vacancies and/or substituting elements were detected for every framework and guest site. Structural and phase purity determinations by powder and single crystal X-ray diffraction alone may not suffice to establish an actual composition and crystal structure for a clathrate. As discussed in **Chapter 5**, tiny variations in the composition of a clathrate will significantly alter its electron count and properties. For example, two different compositions were reported for binary clathrates in the Rb-Sn system: $\text{Rb}_8[\text{Sn}_{44}\square_2]$ and $\text{Rb}_8[\text{Sn}_{44.6}\square_{1.4}]$ [Zhao1994, Kaltzoglou2008c]. While the former composition is electron-balanced, the latter one is not. Such a small variation in the vacancy concentration has a drastic impact on the properties of the material. Even for ideal crystals, which diffract perfectly, it is impossible to resolve cases of joint occupancy of one atomic position with either: three different atom types or two different elements and vacancies. To perform a refinement in such cases, an external compositional constraint is required. The most common technique is to use an elemental composition, determined by energy (or wavelength) dispersive X-ray analyses coupled to scanning electron microscopy. Such analytical methods are very helpful in the detailed investigations of the isothermal cross-sections of the ternary phase diagrams. *Rogl et al.* reported a number of comprehensive phase diagram studies for tetrel clathrates containing transition metals in the framework [Zeiringer2012, Falmbigl2012, Falmbigl2013, Zeiringer2014, Zeiringer2015]. Note that bulk analytical techniques such as ICP (inductively coupled plasma) need to be used with care, since in many cases the samples may contain admixtures of minority phases that will prevent the accurate determination of a clathrate composition. A more reliable way of resolving such complex structures is to combine X-ray diffraction with another diffraction method, such as neutron diffraction. The simultaneous refinement of neutron and X-ray scattering datasets allows for a reliable determination of complicated site occupancies. Neutron diffraction techniques are also extremely helpful for establishing a distribution of two neighboring elements, such as Ga/Ge or Si/P over several crystallographic sites [Christensen2006, Zaikina2010]. The main drawbacks of neutron diffraction are the limited availability of beamtime at neutron facilities and the requirement of large scale samples, although the latter requirement is not as crucial nowadays due to the development of spallation neutron sources. An alternative approach is to use resonant X-ray scattering which was successfully applied to determine complex crystal structures with several crystallographic sites occupied by neighboring elements [Wilkinson2002, Zhang2005]. This technique still requires an access to synchrotron X-ray source. For the substitution in clathrate frameworks, applying characterization techniques which can probe local structure allows for establishing the number of sites, site symmetry, and the type of chemical environment of a particular dopant. Such methods include element specific techniques, such as solid state NMR and NQR, Mössbauer spectroscopy, and EXAFS, as well as non-element specific techniques such as pair distribution function (PDF) and transmission and scanning-transmission electron microscopy (TEM and STEM).

7.2. Superstructures and hidden order in clathrates

Two types of superstructural ordering are reported for clathrates: *translationengleich* and *klassengleich*. The simpler of the two is *translationengleich* ordering, where all of the main translations in the lattice are preserved between the substructure and the superstructure, but there is an overall decrease in the symmetry [Müller2013]. Two examples of this type of transition are the clathrate-VII systems of $\text{Ba}[\text{M}_2\text{P}_4]$, $\text{M} = \text{Ni}, \text{Pd}$. As mentioned in Chapter 3.4, clathrate-VII has an ideal cubic symmetry of $Im\bar{3}m$. Due to the segregation of transition metal and phosphorus atoms over different framework positions, there is a reduction of the symmetry to either a tetragonal $I4/mmm$ or an orthorhombic $Immm$ structure [Keimes1995, Johrendt1994]. Other examples of *translationengleich* ordering can be found in the cationic clathrate-I systems of the general formula $[\text{Ge}_{38}\text{Pn}_8]\text{X}_8$, $\text{Pn} = \text{P}, \text{As}, \text{Sb}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$; and in the $[\text{Si}_{38}\text{Te}_8]\text{Te}_8$ clathrate [von Shnering1972, Menke1973, Jaussaud2004]. In those cases, due to the ordering of tetrel and pnictogen or tellurium atoms over different framework positions, the symmetries are reduced from their ideal clathrate-I space groups, $Pm\bar{3}n$, to lower symmetry space groups, such as $P4\bar{3}n$. The ordering of vacancies in a guest sublattice may also lead to a reduction of the space group symmetry with preserved translations. For example, in the clathrates of $[\text{Si}_{46-x}\text{P}_x]\text{Te}_{8-y}\square_y$, the ordering of Te and vacancies results in a loss of the n -glide plane and a reduction of the symmetry from $Pm\bar{3}n$ to $Pm\bar{3}$ [Zaikina2009].

The ordering of vacancies in a clathrate framework or the segregation of atoms with significantly different chemical natures over different framework positions may also lead to an enlargement of the unit cell size, while the overall clathrate structure is preserved. The reported examples of such superstructures only relate to the clathrate-I structure type. Structural ordering in which the subgroup and the supergroup belong to the same crystal class, but one has fewer translations than the other, *i.e.* lower symmetry, is called *klassengleich* [Müller2013]. In clathrates, an example of this type of ordering can be seen in the clathrate-I family of compounds with $\text{Cs}_8\text{Sn}_{44}\square_2$ and $\text{Ba}_8\text{Ge}_{43}\square_3$ as typical examples. In these systems, two phases exist: the low-temperature phase with an ordered supercell and the high-temperature phase with a disordered subcell. The difference between the two is a *klassengleiche* transition which changes the regular clathrate-I symmetry from $Pm\bar{3}n$ to $Ia\bar{3}d$ for the high- and low-temperature phases, respectively. As indicated in Table 7.1, in this system, the symmetry change is accompanied by a doubling of the unit cell parameters in all directions, increasing the number of atomic framework sites from three in the smaller cell to five in the larger cell [Kaltzoglou2008c, Carrillo-Cabrera2004].

A combination of *translationengleich* and *klassengleich* transitions may be caused by the segregation of the framework atoms over different crystallographic positions. In the cases of the tetrel-free clathrates $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$ and $\text{Ba}_8\text{Au}_{16}\text{P}_{30}$ the lowering of the symmetry from $Pm\bar{3}n$ to $Pbcn$ is accompanied by an increase in the unit cell volume [Dünner1995, Kovnir2011b, Fulmer2013].

A summary of the reported ordered clathrate-I unit cells is given in Figure 7.1 and Table 7.1. Such superstructures were detected due to the high contrast in X-ray scattering power between either transition metals and pnictogens or between framework elements and vacancies. One may expect that more superstructures are possible which have not yet been detected due to similarities in the scattering factors of the framework-forming elements.

Table 7.1. Clathrate-I superstructures with increased unit cell volumes.

Formula	Symmetry	Space Group	a	b	c	V	Description	Reference
$\text{Ba}_8[\text{Cu}_{16}\text{P}_{30}]$	ortho-rhombic	$Pbcn$	$\sqrt{2}a_0$	a_0	$2\sqrt{2}a_0$	$4V_0$	Segregation of Cu and P	Dünner1995 Kovnir2011b
$\text{Ba}_8[\text{Au}_{16}\text{P}_{30}]$	ortho-	$Pbcn$	$\sqrt{2}a_0$	a_0	$2\sqrt{2}a_0$	$4V_0$	Segregation	Fulmer2013

	rhombic						of Au and P	
$\text{Ba}_8[\text{Ge}_{43}\square_3]$	cubic	$Ia\bar{3}d$	$2a_o$	$2a_o$	$2a_o$	$8V_o$	Complete ordering of $\square$	Carrillo-Cabrera2004
$\text{A}_8[\text{Sn}_{44}\square_2]$; A = Rb, Cs	cubic	$Ia\bar{3}d$	$2a_o$	$2a_o$	$2a_o$	$8V_o$	Partial ordering of $\square$	Kaltzoglou2008c
$[\text{Sn}_{14}\text{In}_{10}\text{P}_{21.2}\square_{0.8}]\text{I}_8$	tetragonal	$P4_2/m$	$\sqrt{5}a_o$	$\sqrt{5}a_o$	a_o	$5V_o$	Partial ordering of $\square$	Shatruk2001
$[\text{Sn}_{20.5}\square_{3.5}\text{As}_{22}]\text{I}_8$	cubic	$Fm\bar{3}$ or $F23$	$2a_o$	$2a_o$	$2a_o$	$8V_o$	Partial ordering of $\square$	Zaikina2007a

Figure 7.1. Choices of the unit cell for three variants of clathrate-I superstructures.

8. Non-thermoelectric Applications of Clathrates

8.1. Inorganic clathrates as gas storage materials.

Gas hydrates are crystalline solids with a clathrate structure that forms by passing a pressurized gas, such as Xe, H₂, CH₄, CO₂, N₂, *etc.*, through water at temperatures slightly above 0°C. In the crystal structures of gas hydrates, small guest molecules/atoms are trapped inside the oversized cages of three-dimensional frameworks composed of hydrogen-bonded water molecules (Figure 8.1) [Sloan2008]. The interactions within the water framework of gas hydrates and between the framework and guests are predominately due to hydrogen or van der Waals bonding [Jeffrey1984]. Similarly to inorganic clathrates, the size of the guest species defines the topology of the host framework. Clathrate-I, clathrate-II, and clathrate-H are the most common hydrate structures. The last structure type, clathrate-H, is not found among inorganic clathrates. In contrast to most of their inorganic clathrate cousins, both the water frameworks and the guest atoms or molecules in gas hydrates are neutral.

Hydrate clathrates are currently being studied for their technological applications, including gas storage. The applications of gas hydrates will be not reviewed here; instead we refer interested readers to recent reviews on the topic [Sum2009, Chatti2005, Eslamimanesh2012, Koh2009, Sloan2008, Veluswamy2014].

Figure 8.1. A sample cage from a water-methane clathrate hydrate. O: red; H: grey; C: black.

The primary difference between gas hydrates and inorganic clathrates is the type of host-framework interactions, *e.g.* ionic interactions in the inorganic clathrates are dictated by the host-framework charge transfer. The theoretically predicted clathrate-II Xe₂₄Sn₁₃₆ [Karttunen2014] and the experimentally obtained clathrate-I A_{8-x}(H₂)_ySi₄₆ (A = Na, K) [Neiner2007, Neiner2010] are two examples of inorganic clathrates with neutral guests and they can be considered a link between gas hydrates and inorganic clathrates. According to high-level quantum-chemical calculations, the hypothetical guest-free Sn₁₃₆ clathrate-II framework is only 2.6 kJ/mol (per Sn atom) less stable than the diamond-like α -Sn. The incorporation of Xe atoms in the large and small cages is calculated to additionally stabilize the clathrate structure by decreasing the total energy by 9.2 kJ/mol (per Sn atom) due to Xe-Sn van der Waals

interactions in the hypothetical $\text{Xe}_{24}\text{Sn}_{136}$ [Karttunen2014]. No experimental confirmations for this clathrate have been reported so far.

The incorporation of molecular hydrogen into the clathrate-I silicon framework was elucidated on the basis of elemental analysis, solid state ^1H NMR, thermal gravimetry, mass spectrometry, and Fourier transform infrared spectroscopy for $\text{A}_{8-x}(\text{H}_2)_x\text{Si}_{46}$ ($\text{A} = \text{Na}, \text{K}$). The data was shown to be consistent with the model of the molecular hydrogen alternating with A^+ cations ($\text{A} = \text{Na}, \text{K}$) in the guest sites, but not bound to the silicon framework [Neiner2007, Neiner2010].

8.2. Photovoltaic Materials

Photovoltaics (PVs), *a.k.a.* solar cells, are a class of materials that convert solar energy into direct current electricity using suitable semiconductor p/n junctions (Figure 8.2). Silicon, the second most abundant element on Earth, is the most common material on the market used for photovoltaic cells. However, the diamond-like structure of elemental Si has several disadvantages for photovoltaic applications. First of all, diamond silicon is an indirect semiconductor with a band gap of 1.12 eV. While the size of the band gap is in the correct range for photovoltaic applications (a suitable band gap range is 1.1-1.6 eV), the fact that diamond Si is an indirect semiconductor means that it has inefficient light absorption. Therefore, PVs made of diamond Si require significant micron-sized layers of Si. Thus, finding a semiconducting material that is i) made up of earth abundant elements, ii) compatible with existing silicon technology, and iii) an efficient visible light absorber, likely due to a direct band gap of around 1.4 eV, is important for the development of solar energy harvesting and optoelectronics. Other desired properties of PVs include low recombination rates, high charge carrier mobilities (*i.e.* mobilities of electrons and holes), and broad stability over a wide temperature range, including environmental stability against air and moisture.

Figure 8.2. Schematic representation of the photovoltaic cell.

Due to their complex structures, clathrates of Group 14 (tetrel) elements may offer these desired properties by enabling a new degree of band gap tunability. From among all of the tetrel clathrates, silicon clathrates are the first obvious candidates to study for use in photovoltaic devices, considering the importance of silicon in the semiconductor industry. The clathrate-I, $\text{Na}_8\text{Si}_{46}$, and clathrate-II, $\text{Na}_{24}\text{Si}_{136}$, can both be obtained by the decomposition of a NaSi Zintl phase precursor. As described in Chapter 6, this can be performed either thermally, using spark-plasma sintering, or with mild oxidation by a suitable oxidizing agent, such as HCl produced by the decomposition of NH_4Cl . By controlling the synthesis conditions, the sodium atoms can be removed from the host clathrate framework without destroying it, resulting in a nearly empty Si allotrope: Si_{136} clathrate-II [Ammar2004]. The band gap of Si_{136} clathrate-II was computed by several groups using *ab-initio* calculations, though these calculations did not agree on the size of the band gap or whether or not Si_{136} was a direct gap semiconductor (Table 8.1). Many-body Green function (GW) electronic structure calculations were more accurate, and predicted Si_{136} would have a direct band gap of about 1.8 eV [Blase2003, Connetable2004, Baranowski2014]. This estimation

essentially agrees with the experimental data obtained via optical absorption measurements [Himeno2013, Gryko2000].

Further evaluation of this system shows that the band gap of the Si_{136} clathrate-II can be modified by the substitution of Ge into the framework. A guest free Ge_{136} clathrate-II can hence be produced by mild oxidation of $\text{Na}_{12}\text{Ge}_{17}$ via an ionic liquid. The Ge clathrate-II has a measured direct band gap of ~ 0.6 eV [Guloy2006], which is consistent with theoretical predictions [Connétable2010]. The effect of Si-Ge alloying in the clathrate-II structure was studied by *Moriguchi et al.*; they predicted a direct or nearly direct band gap of 1.2 eV to 2.0 eV for all compositions over the range of alloys from Ge_{136} to Si_{136} , respectively [Moriguchi2000b]. This was further confirmed by theoretical and experimental work performed by *Baranowski et al.*, where a series of $\text{Si}_{136-x}\text{Ge}_x$ clathrate-II materials were synthesized by the thermal decomposition of $\text{NaSi}_{1-x}\text{Ge}_x$ precursors in a specially-designed cold-wall reactor [Baranowski2014]. Their work shows that increasing the Ge content of the clathrate ($\text{Si}_{1-x}\text{Ge}_x$)₁₃₆ causes a shift of the absorption edge to lower energies: 1.7 eV for $x = 0.1$ and 1.2 eV for $x = 0.75$. The absorption onsets of the Ge_{136} and Si_{136} clathrates were determined to be 0.65 eV and 2.2 eV, which is in line with theoretical calculations [Moriguchi2000b, Connétable2010, Baranowski2014, Martinez2013]. Furthermore, silicon clathrate-II thin films were prepared by the reaction of Na vapor with the surface of diamond Si, followed by a thermal decomposition of the obtained Na-Si precursor. Remarkably, preliminary optical data for this material indicates that a film thickness of 2–3 μm should result in $>95\%$ light absorption [Martinez2013].

Another candidate for photovoltaic applications is the clathrate-I $\text{K}_8\text{Al}_8\text{Si}_{38}$, which is composed of inexpensive, earth abundant elements [He2014a]. Theoretical calculations predict a band gap of 1.0 eV, which is consistent with the measured optical band gap of 1.3 eV obtained via UV-Vis spectroscopy. Calculations also predict a semiconducting behavior for the Zintl compositions: $\text{K}_x\text{Al}_x\text{Si}_{46-x}$, $x = 6, 7$, and 8 , with an increase in the band gap as x decreases. In $\text{K}_8\text{Al}_8\text{Si}_{38}$, the calculated electron and hole mobilities are higher than those of amorphous silicon, but they are still ~ 6 -13 times smaller than those of crystalline silicon. In addition to band gap size and mobilities, another key property for photovoltaic materials is the spatial localization of electrons and holes, which was investigated for $\text{K}_8\text{Al}_8\text{Si}_{38}$ by computing square moduli for the top valence band wavefunction (VBM) and for the bottom conduction band wavefunction (CBM). It was predicted that the VBM is localized around the Al atoms of the large 24-vertex cages of the clathrate-I structure, while the CBM is localized around the Si atoms of the small 20-vertex cages. This indicates a limited spatial overlap, resulting in a low probability of charge recombination.

As it was suggested earlier, the ability to tune the band gap of potential PV materials would be quite useful in developing ideal PV materials. Such band gap tailoring was computationally explored for the Si_{46} clathrate-I. In this example, all guest sites were filled with either the electronegative halogen I, the inert gas Xe, or the tetrel Sn [Connétable2001]. It was observed that, depending on the identity of the guest atom, the electronic properties changed from a wide gap semiconductor ($\text{Xe}_8\text{Si}_{46}$, $E_g = 2.25$ eV) to a metal in the case of the hypothetical $\text{Sn}_8\text{Si}_{46}$. Furthermore, 44 metastable Si allotropes with cage-like structures were theoretically predicted, of which 11 exhibited direct or quasidirect band gaps in the range of 1.0–1.8 eV, making them suitable for photovoltaic applications [Amsler2015]. These low-density silicon allotropes are based on Si polyhedral cages made of 14 to 40 Si atoms with faces of 4-, 5-, 6-, 7-, and 8-membered rings, in many ways similar to clathrate structures. The new silicon allotrope, Si_{24} , was obtained by the thermal “degassing” of Na from the high-pressure binary phase, $\text{Na}_4\text{Si}_{24}$ [Kurakevych2013, Kim2015a]. The non-clathrate structure of $\text{Na}_4\text{Si}_{24}$ features channels of tetrahedrally-bound silicon atoms hosting Na guest atoms. Upon the removal of Na, the structure is preserved; leading to the new Si_{24} allotrope of silicon, which is only stable up to $\sim 450^\circ\text{C}$. Si_{24} features a quasidirect band gap (nearly degenerate indirect and direct gaps) of approximately 1.3 eV, which makes it a promising candidate for thin-film solar applications. However, the synthesis of Si_{24} allotrope requires a high-pressure precursor, which limits the synthesis scalability. Thus, the exploration of new synthetic routes is needed to obtain potentially useful Group 14 allotropes, both in the bulk form and in the form of thin film devices. While theoretical predictions on this subject are important and relevant, experimental verification

is also necessary to characterize the sizes and types of the band gaps, the recombination rates, and mobilities of the electrons and holes.

Table 8.1. Calculated and experimental bandgap for Si and Ge clathrates.

Clathrate	Band gap, eV and its type	Method used	Reference
$\text{Na}_x\text{Si}_{136}$	1.6–1.8 eV (direct) 1.1–1.2 eV (indirect)	Diffuse reflectance spectroscopy	Himeno2013
Ge_{136}	0.6 eV (direct)	Diffuse reflectance spectroscopy	Guloy2006
Si_{136} Si_{46}	2.3 eV(indirect) 2.3 eV(nearly direct)	DFT within generalized gradient approximation (GGA)	Conesa2004
Si_{136}	1.9 eV	electrical conductivity and optical absorption measurements	Gryko2000
Si_{136} Si_{46}	1.9 eV, indirect	DFT within the local density approximation (LDA)	Adams1994
$\text{Na}_4\text{Si}_{136}$ $\text{Na}_4\text{Si}_{136}$	1.2 eV, indirect 1.2 eV, indirect	DFT within the local density approximation (LDA)	Demkov1994
Si_{136} Ge_{136}	1.9 eV, direct 1.2 eV, direct	<i>ab-initio</i> pseudopotential theory within the LDA	Moriguchi2000b
Si_{136}	1.85 eV direct	DFT-LDA or GW calculations	Blase2003
Si_{136}	1.85 eV direct	GW calculations	Connétable2004
Si_{136} Ge_{136}	1.8 eV 0.8eV	Many-body Green function (GW) electronic structure	Martinez2013
Si_{136}	2.14 eV nearly direct	Hybrid Heyd–Scuseria–Ernzerhof (HSE) exchange–correlation functional within the plane-augmented-wave (PAW) formalism (VASP)	Baranowski2014

8.3. Superconductors

The majority of clathrate superconductor research has been in the area of silicon clathrates, more specifically, in the area of Si clathrate-I. As such, little information on the superconductivity of clathrates of other types is available. We refer interested readers to a recent comprehensive review by *Yamanaka et al.* on high pressure synthesis and the superconductivity of clathrates [Nolas2014]. Here we only briefly describe examples of superconducting clathrates.

The discovery of superconductivity in the alkali-metal-doped fullerenes, K_3C_{60} (transition temperature, $T_c = 19.5$ K) and $\text{RbCs}_2\text{C}_{60}$ ($T_c = 33$ K), with the lightest group 14 element, initiated the search for superconductivity in other group 14 framework compounds, including clathrates. In 1995, *Yamanaka* and co-workers reported on the discovery of the first superconductors in the clathrate family, $\text{Na}_x\text{Ba}_6\text{Si}_{46}$ with $T_c \sim 4$ K [Kawaji1995], and $\text{K}_x\text{Ba}_6\text{Si}_{46}$ with $T_c \sim 3.2$ K [Yamanaka1995]. These type I clathrates were obtained by thermal decomposition of the mixed-cation Zintl precursors, Na_2BaSi_4 and K_2BaSi_4 , in a dynamic vacuum. In the structure of $\text{Na}_x\text{Ba}_6\text{Si}_{46}$, the barium cations almost fully occupy the larger 24-vertex cages, while the smaller sodium cations only partially occupy the 20-vertex cages (pentagonal dodecahedra) of the silicon framework. By further heat treatment of $\text{Na}_x\text{Ba}_6\text{Si}_{46}$, fully Na-depleted compositions can be obtained. In this system, the T_c increases as the Na content in the smaller dodecahedral cages decreases, reaching a maximum of ~ 4.8 K for $\text{Na}_{0.2}\text{Ba}_6\text{Si}_{46}$.

Additionally, the subsequent heat treatment of $\text{Na}_{0.2}\text{Ba}_6\text{Si}_{46}$ with Na vapor enriches the clathrate phase with Na, resulting in a decrease of the T_c down to 2.8 K for $\text{Na}_{0.7}\text{Ba}_6\text{Si}_{46}$ [Kawaji1996]. Furthermore, the absence of Ba in the clathrate-I, *i.e.* $\text{Na}_8\text{Si}_{46}$, results in metallic properties with no signs of superconductivity down to ~ 2 K. The same is true for the Ba-free clathrate-II, $\text{Na}_x\text{Si}_{136}$, which was also

shown to exhibit similar non-superconducting metallic properties [Roy1992]. Conversely, high-pressure high temperature (HPHT) conditions (3 GPa at 1073 K) can be used to fully substitute Ba for Na in the Si clathrate-I, which results in higher transition temperatures of 8-9 K for $\text{Ba}_x\text{Si}_{46}$ [Yamanaka2000, Fukuoka2003b]. $\text{Ba}_x\text{Si}_{46}$ with a slight Ba deficiency, $x = 7.76$, shows the highest T_c of 9 K. Here, the smaller cage is only 88% occupied. Subsequent annealings under vacuum remove the barium from the smaller cage, resulting in a decrease in the T_c down to 6 K when the smaller cage is only 32% occupied by Ba. The population of the smaller cage in the Si_{46} clathrate-I framework with Ba or Na has an opposite effect on the T_c .

The metallic behavior of $\text{Na}_8\text{Si}_{46}$ can be explained by theoretical calculations of the band structure [Moriguchi2000a]. Within the rigid band model, the electrons donated from Na atoms fill the conduction band of Si_{46} , and the Na bands are located at the bottom of the Si conduction band. In contrast, Ba 5d states in $\text{Na}_2\text{Ba}_6\text{Si}_{46}$ and $\text{Ba}_x\text{Si}_{46}$ are strongly hybridized with the valence states of the Si framework. This leads to a peak in the density of states at the Fermi level: a fingerprint of superconductivity [Moriguchi2000a, Saito1995, Connétable2003]. ^{29}Si , ^{23}Na , ^{137}Ba , and ^{135}Ba NMR studies on the superconducting phase $\text{Na}_x\text{Ba}_6\text{Si}_{46}$ confirmed its metallic nature, and revealed that Na and Ba guests are not fully ionized [Shimizu1996]. The hybridization of Ba 5d and Si 3p states was further confirmed by Compton scattering studies of $\text{Ba}_8\text{Si}_{46}$ as well as by ultrahigh-resolution photoemission spectroscopy experiments [Yokoya2001]. Furthermore, a study of isotope effects on the superconductivity of $\text{Ba}_8\text{Si}_{46}$, along with Raman scattering, provides evidence that the Ba-Si clathrate is a phonon-mediated superconductor, where a high density of states at the Fermi level is attributed to the hybridization of Ba 5d and Si framework orbitals [Tanigaki2003]. A combined theoretical and experimental study of several Si-doped clathrates, $\text{Na}_8\text{Si}_{46}$ and $\text{Ba}_8\text{Si}_{46}$ in particular, explained the acoustic excitation of the Ba guest sub-network [Reny2002]. Inelastic neutron scattering with X-ray absorption spectroscopy and *ab initio* calculations pointed out the importance of the host-guest vibrational coupling between Ba atoms with the Si_{24} cage. In the Na systems, the rattling of Na atoms inside the Si cages leads to strong anharmonicity, which results in a weaker coupling of Na atoms with the host lattice. From these studies, it was proposed that the enhancement of T_c could be achieved by substituting larger ionic guests into the Si_{24} cage [Reny2002]. Interestingly, an experimental study of the electron-rich $\text{Cs}_{7.3}\text{Si}_{46}$ clathrate-I obtained via HPHT, with large Cs^+ guest cations, did not show any superconductivity down to 2 K [Wosylus2009].

Unfortunately, any and all alterations to the $\text{Ba}_x\text{Si}_{46}$ system reported to date have led to a decrease in the T_c . Several examples of the fading of superconductivity upon substitution into the $\text{Ba}_{8-x}\text{Si}_{46}$ are given below. The T_c gradually decreases from 8.0 K for $\text{Ba}_{7.6}\text{Si}_{46}$ to 2.2 K for $\text{Ba}_{8-\delta}\text{Si}_{23}\text{Ge}_{23}$ with increasing Ge content in $\text{Ba}_{8-\delta}\text{Si}_{46-x}\text{Ge}_x$ ($0 \leq x \leq 23$) prepared under HPHT [Fukuoka2003a]. Each of the samples has a slight Ba deficiency, which is irrespective of the Ge content, thus this is unlikely to be the reason for the lowering of T_c . Since the superconductivity of $\text{Ba}_{8-\delta}\text{Si}_{46}$ was shown to be driven by a phonon-mediated mechanism, an increase in the average covalent bond distances in the framework due to Ge substitution depresses the phonon-electron interactions, and leads to a decrease in the T_c . Furthermore, when the Ge content exceeds 50%, superconductivity disappears due to the increased concentration of defects in the 6c site, which interrupt the conduction path of electrons.

The superconductivity in $\text{Ba}_x\text{Si}_{46}$ can also be quenched by transition metal substitution into the Si framework, such as in $\text{Ba}_8\text{T}_x\text{Si}_{46-x}$, where T is a Group 11 transition metal (Au, Ag, or Cu). In these systems, the transition metals preferentially occupy the 6c sites of the framework's larger 24-vertex cages. It is interesting to note that, unlike the parent phase BaSi_{46} , the presence of transition metals in $\text{Ba}_8\text{T}_x\text{Si}_{46-x}$ allows the phase to be stabilized without the need for high pressure. For very small concentrations of T, *i.e.* $x = 1$, the superconducting volume fraction increases up to ~50% and the critical temperatures range from 5 to 6 K depending on the type of transition metal [Herrmann1998]. By a combination of soft X-ray photoemission spectroscopy and band structure calculations, it was shown that doping Ag into the silicon framework of $\text{Ba}_8\text{Si}_{46}$ reduces the density of states at the Fermi level due to a decrease in the charge carrier concentration. This also leads to a decrease in the T_c [Kamakura2005, Nozue2000]. A similar conclusion for the drop in T_c of $\text{Ba}_8\text{Cu}_x\text{Si}_{46-x}$ was derived by using first-principles DFT calculations [Li2005].

Group 10 transition metals, such as Ni, also suppress the superconductivity in $\text{Ba}_8\text{Si}_{46}$. The metastable clathrates $\text{Ba}_{7.9}\text{Ni}_x\text{Si}_{46-x}$, with $x = 1.6$ and 1.4 , prepared by a fast cooling of the melts between two steel plates, show superconducting transitions with onsets at $T_c = 6$ and 5.5 K, respectively. Similar to its superconducting parent phase, $\text{Ba}_{8-x}\text{Si}_{46}$, structure refinements of powder X-ray diffraction data indicate the 20-vertex cage is only partially occupied by Ba, and like Group 11 framework substitutions, Ni atoms preferentially sit in the 6c framework sites. The lowering of the T_c in $\text{Ba}_{7.9}\text{Ni}_x\text{Si}_{46-x}$ was attributed to a decrease in the electron–phonon coupling strength that originates from the Ni content variations resulting in the alternation of the electronic band structure [Aydemir2012].

The substitutions of Si with Group 13 elements, such as Al, show a similar trend: T_c systematically decreases with an increase in the Al content. For $\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$, where $x = 3$, a T_c of ~ 6 K was reported, while a lower T_c of 3 K was measured for $x = 8$. Similarly to the aforementioned transition metal substitutions, the suppression of superconductivity in these phases was attributed primarily to a decrease in the density of states at the Fermi level [Li2013, Li2015b, Liu2014]. An analogous decrease of T_c was reported for the Ga-substituted clathrate $\text{Ba}_8\text{Ga}_6\text{Si}_{40}$ ($T_c = 3.3$ K). For Ga concentrations exceeding $x = 10$, no superconductivity was observed down to 1.8 K [Li2007].

Furthermore, an even more pronounced suppression of superconductivity is observed upon the substitution of Ba for the smaller magnetic Eu^{2+} cation. Samples of $\text{Ba}_{8-x}\text{Eu}_x\text{Al}_6\text{Si}_{40}$ with $x > 0.5$ do not exhibit any superconducting transition above 2 K, and the development of ferromagnetic correlations between Eu^{2+} magnetic centers was proposed as the cause of the suppression of superconductivity [Liu2015].

Upon isovalent substitution of Ba with smaller Sr atoms, the clathrate $\text{Ba}_{8-x}\text{Sr}_x\text{Si}_{46}$ can be formed with $x \leq 6$ using HPHT synthesis, though $\text{Sr}_8\text{Si}_{46}$ cannot be obtained [Toulemonde2005]. Smaller Sr atoms preferentially occupy the smaller cages in the clathrate-I structure for x up to 2, then, with an increase in the overall Sr content above 2, the Sr atoms mix with Ba atoms in the larger cages. For all refined compositions, the smaller cage is only partially occupied by Sr up to 89%. As expected, Sr substitution leads to shrinkage of the unit cell's volume due to the shortening of guest-framework distances, while Si-Si bond distances only slightly change. Sr substitution results in a reduction of T_c down to 4 K for $x = 6$. Since Si-Si distances are almost unchanged, the reduction in T_c cannot be attributed to the weakening of electron-phonon interactions as was the case for $\text{Ba}_{8-\delta}\text{Si}_{46-x}\text{Ge}_x$ ($0 \leq x \leq 23$), and this reduction in T_c must have a different origin. As described earlier, the superconductivity in $\text{Ba}_{8-x}\text{Si}_{46}$ clathrates was suggested to originate from the strong hybridization of Ba 5d orbitals with Si framework orbitals, leading to a high density of states at Fermi level. Calculations of the band structure of the hypothetical $\text{Sr}_8\text{Si}_{46}$ phase sure enough resulted in a lower density of states at the Fermi level than that of $\text{Ba}_{8-x}\text{Si}_{46}$ due to a weaker hybridization between Si orbitals and Sr 4d states. This aligns well with the experimentally-observed vanishing of superconducting properties caused by Sr substitution. Likewise, similar results to those of Sr were also obtained for the Ca-substituted phase $\text{Ba}_{8-x}\text{Ca}_x\text{Si}_{46}$ ($x \leq 4$) [San-Miguel2005].

Thus, the highest superconducting transition temperatures of up to 9 K were reported for the clathrate-I phase $\text{Ba}_{8-x}\text{Si}_{46}$, and any substitution into the framework or guest sites thus far has resulted in a suppression of the superconductivity. However, there are multiple causes of this suppression, therefore different concentrations of different substituent elements are needed to completely quench superconductivity (Table 8.2).

Aside from the silicon clathrate-I, superconductivity was also identified in the clathrate-IX $\text{Ba}_{24}\text{Si}_{100}$ (T_c of ~ 1.5 K) which has a helical structure [Viennois2005, Rachi2005]. It was shown that $\text{Ba}_{24}\text{Si}_{100}$ is a second type of superconductor with moderate electron–phonon interactions. Clathrate-IX is a rare example of a clathrate containing not only tetrahedrally-coordinated, and thus formally sp^3 -hybridized Si atoms, but also three-coordinated, and therefore sp^2 -hybridized Si atoms. Since the strong electron–phonon coupling inside the larger Si_{24} cages, as well as sp^3 bonding, were proposed to be crucial for the superconductivity of Si clathrates [Connétable2003, Shimizu1996], the higher T_c for clathrate-I, $\text{Ba}_{8-x}\text{Si}_{46}$, versus clathrate-IX, $\text{Ba}_{24}\text{Si}_{100}$, was attributed to the maximization of sp^3 character in the silicon framework and to the subsequent enhancement of its electron-phonon coupling [Viennois2005].

Additionally, high pressure was shown to suppress the superconducting transition of $\text{Ba}_{24}\text{Si}_{100}$, though no structural transition was detected up to 1.7 GPa and irreversible amorphization occurs above 23 GPa [Shimizu2005, Rachi2005].

Only a few examples of superconductivity in germanium clathrates were reported. Though superconductivity was reported for the clathrate-I $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ (T_c of 7.5 K) [Bryan1999], it was remeasured and disputed later on [Sales2001].

Similar to the silicon analogue, the clathrate-IX $\text{Ba}_{24}\text{Ge}_{100}$, is a curious example of a superconducting clathrate. Unlike its Si analogue, the application of high pressure to the Ge clathrate leads to a 16-fold enhancement of T_c from 0.24 K at ambient pressure to 3.7 K at 2.7 GPa [Grosche2001, Yuan2002, Yuan2004]. A further increase in the pressure above 2.7 GPa leads to a slight decay of the T_c . At ambient pressure, $\text{Ba}_{24}\text{Ge}_{100}$ was found to undergo a two-step structural phase transition, at ~ 215 K and 180 K. This is associated with the breaking of Ge–Ge bonds along with the random displacement of neighboring Ba atoms into split positions. Quantum-chemical calculations indicate that a sharp peak in the density of states at the Fermi level of $\text{Ba}_6\text{Ge}_{25}$ originates mainly from the Ba $5d$ states, and decreases due to the shifting of barium atoms toward the experimentally-deduced split positions. Thus, this low-temperature structural transition reduces the density of states at the Fermi level and explains the lowered T_c [Zerec2002]. This decrease in the density of states at the Fermi level upon lowering of the temperature was experimentally confirmed by soft X-ray photoelectron spectroscopy and magnetic susceptibility measurements [Tang2010]. The application of high-pressure allows for the stabilization of the low-disorder, high-temperature phase, thus structural phase transitions are suppressed. This inevitably leads to an increase in the density of states at the Fermi level, which results in 16-fold enhancement of T_c .

Na substitution for Ba in the Ge clathrate-IX was also studied, and an isostructural clathrate, $\text{Na}_8\text{Ba}_{16}\text{Ge}_{100}$, can be formed. In this case, Na and Ba atoms share the open zeolite-like channel sites in between the helical chains of pentagonal dodecahedra, while the positions inside the dodecahedra are solely occupied by Ba atoms. $\text{Na}_8\text{Ba}_{16}\text{Ge}_{100}$ becomes a superconductor at $T_c \approx 1.05$ K (ambient pressure), and unlike $\text{Ba}_{24}\text{Ge}_{100}$, no structural distortion was observed upon a lowering of the temperature [Grosche2001, Yuan2002, Yuan2004].

Remarkably, no superconductivity has been reported for tin clathrates thus far. A superconducting onset at 3.7 K is frequently observed in the low temperature/low field magnetic susceptibility measurements of tin clathrates, but this is attributed to traces of β -Sn [Zaikina2007b, Kaltzoglou2008a, Kaltzoglou2008c].

Superconductivity was also reported for clathrate-like compounds, such as $\text{Ba}_3\text{Ir}_4\text{Ge}_{16}$, BaIr_2Ge_7 , and $\text{Ba}_3\text{Rh}_4\text{Ge}_{16}$, with $T_c = 6.1$, 3.2, and 6.5 K, where Ba occupy edge-shared, crown-shaped Ge_{16} polyhedra. Another interesting example of a superconductor with a cage-like structure is the theoretical calcium hydride, CaH_6 , which was predicted to have a T_c of 220–235 K at 150 GPa. Its structure and superconducting properties were theoretically predicted by *ab-initio* quantum chemical calculations. The cubic $Im\bar{3}m$ structure consists of interlocking H_4 units which form a sodalite framework with a Ca atom encapsulated in the cage. This is actually an example of the undistorted clathrate-VII structure [Wang2012].

Table 8.2. Superconducting properties of inorganic clathrates.

Clathrate composition	Type	T_c , K	Reference
$\text{Ba}_8\text{Si}_{46}$	clathrate-I	8	Yamanaka2000
$\text{Ba}_{7.76}\text{Si}_{46}$	clathrate-I	9	Fukuoka2003b
$\text{Ba}_{6.63}\text{Si}_{46}$		6	
$(\text{NaBa})_x\text{Si}_{46}$	clathrate-I	4	Kawaji1995
$(\text{KBa})_x\text{Si}_{46}$ with T_c	clathrate-I	3.2	Yamanaka1995
$\text{Na}_{1.5}\text{Ba}_6\text{Si}_{46}$	clathrate-I	2.6	Kawaji1996
$\text{Na}_{0.3}\text{Ba}_{6.2}\text{Si}_{46}$		4	
$\text{Na}_{0.2}\text{Ba}_{6.0}\text{Si}_{46}$		4.8	

$\text{Ba}_8\text{T}_x\text{Si}_{46-x}$, $x < 1$ T = Au, Ag, Cu	clathrate-I	5-6	Herrmann1998
$\text{Ba}_8\text{Ag}_1\text{Si}_{45}$ $\text{Ba}_8\text{Ag}_3\text{Si}_{43}$	clathrate-I	7 2.8	Kamakura2005
$\text{Ba}_8\text{Cu}_4\text{Si}_{42}$	clathrate-I	2.9	Li2005
$\text{Ba}_{7.9}\text{Ni}_{1.4}\text{Si}_{44.6}$ $\text{Ba}_{7.9}\text{Ni}_{1.6}\text{Si}_{44.4}$	clathrate-I	6 5.5	Aydemir2012
$\text{Ba}_{8-x}\text{Si}_{46-x}\text{Ge}_x$ ($0 \leq x \leq 23$) $x = 6$ $x = 15$ $x = 18$ $x = 23$	clathrate-I	6 4 3 - -	Fukuoka2003a
$\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$ $x = 4$ $x = 6$ $x = 3$ $x = 4$ $x = 5.5$ $x = 6.5$ $x = 7$ $x = 8$	clathrate-I	5.5-5.7 4.7 6 5.7 6.3 5.5 3.5 3.3	Li2013, Li2015b Li2013 Liu2014
$\text{Ba}_8\text{Ga}_6\text{Si}_{40}$	clathrate-I	3.3	Li2007
$\text{Ba}_{8-x}\text{Sr}_x\text{Si}_{46}$ $x = 1.8$ $x = 4.6$ $x = 5.7$	clathrate-I	7.2 5.3 4.1	Toulemonde2005
$\text{Ba}_{8-x}\text{Ca}_x\text{Si}_{46}$ $x = 1$ $x = 2$ $x = 4$	clathrate-I	7.7 5.3 3.7	San-Miguel2005
$\text{Ba}_{8-x}\text{Eu}_x\text{Al}_{5.3}\text{Si}_{40.7}$ $x = 0.07$ $x = 0.67$	clathrate-I	4.2 -	Liu2015
$\text{Ba}_{24}\text{Si}_{100}$	clathrate-IX	1.5	Viennois2005 Rachi2005
$\text{Ba}_{24}\text{Ge}_{100}$	clathrate-IX	~0.24 3.8 (at 2.7 GPa)	Grosche2001, Yuan2002, Yuan2004
$\text{Na}_8\text{Ba}_{16}\text{Ge}_{100}$	clathrate-IX	~0.84	Grosche2001

8.4. Li-battery anodes

In rechargeable lithium ion batteries, the properties desired for a good anode material include: a high specific capacity, low and stable potential for reversible Li de-/intercalation, suitable electron and Li ion conductivity, good structural stability upon de-/intercalation provided by a flexible open structure, and only a moderate volume change upon lithiation. Currently, the material used for battery anodes is graphite, which only has a moderate specific capacity of 372 mAh/g. Diamond Si was briefly considered to be an attractive replacement for the graphite in Li-ion battery anodes due to its high specific capacity

(4200 mAh/g). However, Si anodes suffer from significant volume changes ($> 300\%$) upon electrochemical delithiation, leading the anode to fracture and the battery to fail.

Clathrate structures provide large polyhedral cages that can encapsulate different guest atoms. Thus, they present the possibility of holding the ions necessary for battery cells. Also, as mentioned earlier in the review, some clathrate frameworks are stable both with guest cations and without them, possibly providing the structural flexibility battery anodes need to survive cycling. The synthesis of a clathrate with intercalated lithium was studied by *Langer et al.* in 2012, and ultimately proven plausible. The clathrate-II $\text{Na}_x\text{Si}_{136}$ ($x \rightarrow 0$), featuring eight hexakaidecahedra cages and 16 pentagonal dodecahedra cages per unit cell, is one example of a clathrate which is almost guest-free. As such, it was investigated as a potential material for Li battery anodes. A $\text{Na}_{1.3}\text{Si}_{136}$ was obtained by the controlled decomposition of a NaSi Zintl phase precursor under vacuum. In battery tests for this material, a potential (voltage) plateau was observed at 300 mV (vs. Li/Li^+), different from the plateau for elemental silicon at 110 mV. *Ex-situ* powder XRD studies revealed that the clathrate structure was preserved within the potential plateau at around 300 mV with a specific capacity corresponding to ~ 24 Li atoms per unit cell of Si_{136} , which is equivalent to the total number of polyhedral cages per unit cell. Upon a further insertion of lithium at the potential range of 250-100 mV, the clathrate structure first “collapses” to an amorphous phase and subsequently transforms into the metastable crystalline $\text{Li}_{15}\text{Si}_4$ phase at a deep charge down to 20 mV. This two-step formation of Li-Si binary is similar to what has been observed for diamond Si electrodes. ^7Li solid state magic angle spinning-nuclear magnetic resonance (MAS-NMR) data of the electrochemically-lithiated clathrate $\text{Li}_y\text{Na}_x\text{Si}_{136}$ ($x \rightarrow 0$, $y \rightarrow 24$) shows two resonances at 412 and 433 ppm, even after the resonance from any residual electrolyte is excluded from the spectrum. These chemical shifts cannot be attributed to any known binary lithium silicides. Additionally, they occur in a 2:1 ratio. Thus, they can be assigned to the Li atoms in both the larger 28-vertex cages (Wyckoff site 16c) and the smaller 20-vertex cages (Wyckoff site 8b) of the clathrate-II $\text{Na}_x\text{Si}_{136}$ ($x \rightarrow 0$) structure. Furthermore, these observed shifts are significantly larger than the resonance shifts of pure Li metal (270 ppm). Similarly, the ^{23}Na solid state MAS-NMR chemical shifts for the $\text{Na}_x\text{Si}_{136}$ clathrate are in the range of 1500-2100 ppm, which are larger than the chemical shifts for pure sodium metal (1131 ppm). The larger chemical shifts for the guest cations (Li or Na) than their respective metals were attributed to a Knight shift caused by a strong hyperfine interaction of their nuclear spins with unpaired conduction electrons. This explanation is in line with a non-charge-balanced composition and likewise aligns with the expected metallic behavior of alkali-metal doped Si_{136} clathrates, where the electrons donated by alkali-metal guests populate the conduction band. This ^7Li NMR study of electrochemically-lithiated electrodes containing the $\text{Na}_x\text{Si}_{136}$ ($x \rightarrow 0$) clathrate conclusively proves that the $\text{Li}_y\text{Si}_{136}$ ($y \rightarrow 24$) clathrate-II can be obtained electrochemically, producing a structure where Li solely fills all the cages of the clathrate framework. Unfortunately, the irreversible structural collapse during its lithiation/delithiation means this structure is unsuitable for battery applications as it is currently [Langer2012].

“Empty” silicon or germanium clathrates are metastable with respect to their ground state, face-centered cubic, α -phases of a diamond structure, *i.e.* α -Si and α -Ge. First-principles density functional theory (DFT) calculations showed that the intercalation of Li into the empty cages of the clathrate-II Si_{136} did not sufficiently compensate for the energy difference between the empty clathrate and the α -Si phase, presenting a possible explanation for the observed structural collapse upon lithiation. It was proposed that the empty clathrate structure could potentially be stabilized by the addition of Ba guest atoms. A trend in the calculated formation energies upon the step-wise encapsulation of Li atoms into the smaller 20-vertex cages of the clathrate-II structure indicated that this process is energetically favorable, as it resulted in an overall decrease in the formation energy of $\text{Li}_x\text{Si}_{136}$ as x increased up to 24. However, the theoretical formation energy of $\text{Li}_{24}\text{Si}_{136}$, where all of the cages are filled by Li atoms, is still positive, making $\text{Li}_{24}\text{Si}_{136}$ less stable than its decomposition into Li and α -Si. Thus, it was proposed that additional guest atoms filling the larger 28-vertex cages might stabilize this clathrate structure, and the smaller 20-vertex cage could be filled with Li. However, this was not the case for the clathrate $\text{Na}_8\text{Si}_{136}$ in which all of the larger cages are filled by Na atoms. Calculations predicted this clathrate to be less stable than the

respective α -Si and Na elements. Conversely, for the barium-containing clathrate $\text{Ba}_x\text{Si}_{136}$ with $x > 6$, the formation energy became negative, thus making it more stable with respect to its decomposition into α -Si and Ba metal. Further calculations of the $\text{Li}_y\text{Ba}_8\text{Si}_{136}$ clathrate pointed out that the occupation of the smaller cage in the clathrate structure with Li atoms is energetically favorable. Likewise, the calculated volume change upon Li intercalation into $\text{Ba}_8\text{Si}_{136}$ is negligibly small (0.002%) compared to other anode materials such as graphite (10%) or silicon (>300%). This behavior was attributed to the rigidity of the Si clathrate framework, and it is beneficial for a reduction of the capacity fading during charge–discharge cycles. The theoretical calculations are consistent with the Zintl-Klemm formalism, which predicts $\text{Li}_y\text{Ba}_8\text{Si}_{136}$ ($y = 0, 4, 8$) clathrates should exhibit metallic behavior, advantageous for anode applications. The calculated average intercalation voltage for $\text{Li}_y\text{Ba}_8\text{Si}_{136}$ was found to be low (~ 400 mV) and nearly constant, which is beneficial for the design of Li ion batteries with high cell voltages and long lifetimes. A theoretical study of the Li diffusion pathways indicated, for the case of $\square_{16}\text{Ba}_8\text{Si}_{136}$, where all large cages are filled with Ba ions, Li migration occurs between adjacent 20-vertex cages (5^{12}), but not through the centers of their common pentagonal faces. Interestingly, the theoretically-predicted Li diffusion pathway involves the breaking of the Si–Si bond connecting two adjacent 5^{12} cages. This is followed by the formation of Li–Si bonds ($\sim 2.5\text{\AA}$) and a further migration of the Li atom towards the center of the next 5^{12} cage. Finally, the Si–Si bonds are reformed. A similar insertion of the larger alkali metal, Na, into a Sn-based clathrate framework was experimentally observed for an anionic clathrate-III [Bobev2001]. Alternatively, when some of the larger 28-vertex cages ($5^{12}6^4$) are available for the Li ions, as in $\square_{16}\square_2\text{Ba}_6\text{Si}_{136}$, where the large cages are only partially filled by Ba atoms, the Li diffusion is most likely to occur through the common hexagonal face of two adjacent hexakaidecahedra cages.

The theoretically calculated discharge capacity, under an assumption that all of the small cages are filled with Li ions, as in $\text{Li}_{16}\text{Ba}_8\text{Si}_{136}$, was determined to be 85 mAh/g, which is much lower than the maximum capacity for the current graphite anode, 372 mAh/g. The variation in Ba occupancy for this system makes the larger cages available for Li, thus increasing its theoretical capacity. Moreover, theoretically the large $5^{12}6^4$ cages can accommodate up to 3 Li atoms per cage, leading to increased discharge capacities of 123 mAh/g for the hypothetical $\text{Li}_{16}\text{Li}_{2\times 3}\text{Ba}_6\text{Si}_{136}$ clathrate, which matches the capacities of LiCoO_2 and LiFePO_4 cathodes well. Silicon clathrates show much lower theoretical capacities than diamond Si (4200 mAh/g), since, unlike diamond Si, their lithiation does not involve significant changes to the structure. Rather, their lithiation is better described by an intercalation/deintercalation process. Therefore, the changes in the volume upon the intercalation of Si clathrates are not as drastic as they are in the case of diamond Si, which is beneficial for anode manufacturing [Yang2013].

Clathrate-I materials have also been investigated for battery anodes. For example, recently, the electrochemical performance of the $\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$ clathrate-I was experimentally investigated [Li2015c]. Electrodes based on $\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$ clathrates were prepared via either arc melting or a heat treatment of the elements. Surprisingly, an electrochemical capacity was obtained which corresponded to up to 44 Li atoms per unit cell of $\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$. Moreover, the intercalation/deintercalation processes were neither accompanied by a noticeable change in the unit cell parameters, nor did they lead to a change in the Si chemical environment upon clathrate lithiation, as evidenced from *ex-situ* powder XRD and ^{29}Si NMR data, respectively. In turn, the ^7Li chemical shift is similar to those of other Li silicides, particularly that of LiSi , which is in contrast to the aforementioned Li NMR signals observed for intercalates into Si_{136} framework. Further studies are desired, including *in-situ* characterizations to elucidate the mechanism of the Li electrochemical intercalation/deintercalation processes in the $\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$ clathrate.

A theoretical study using first-principles density functional theory (DFT) was recently performed to investigate the preferred structures of low degrees of lithiation in the clathrate-I systems $\text{Ba}_x\text{Si}_{46}$ and $\text{Ba}_x\text{Al}_6\text{Si}_{40}$ [Peng2015]. Trends in their calculated formation energies indicate that Li insertion into the smaller 5^{12} cages has a stabilization effect for the clathrates with Ba-deficiencies in that cage $\square_2\text{Ba}_6\text{Si}_{46}$ and $\square_2\text{Ba}_6\text{Al}_6\text{Si}_{46}$. Interestingly, Li incorporation into the framework was also deemed feasible. This study suggested that the insertion of Li should result in measurable changes in the unit cell volumes, as well as

alterations of the local atomic environments of the framework atoms, in contrast to the experimental observations reported by [Li2015c].

Germanium clathrates, the empty $\square_{24}\text{Ge}_{136}$ clathrate-II in particular, were also considered as anode materials for Li-ion batteries. An unambiguous linear increase in the unit cell parameter of Ge_{136} upon electrochemical lithiation was elucidated by *in-situ* synchrotron powder XRD. In the clathrate-II structure, there are 24 empty cages per unit cell available for filling with Li atoms. Interestingly, after reaching a maximum Li capacity of 24 atoms per unit cell (under the assumption that each cage can be filled by only one Li atom), the unit cell parameter continued to increase up to ~ 110 Li atoms per unit cell. The experimental voltage curve did not feature any clear plateaus which could be assigned to the formation of a second phase and no secondary crystalline phase was detected by XRD. Careful analysis of the powder XRD data revealed that the fraction of crystalline clathrate-II phase decreased for larger degrees of lithiation. An assumption was made that the clathrate partially transforms into an amorphous product. Hence, the tentative lithiation process of the $\square_{24}\text{Ge}_{136}$ clathrate-II can be described as the filling of empty cages in the germanium framework by Li atoms together with a simultaneous transformation of the clathrate phase into other amorphous products. Additionally, the filling of more than one Li atom per cage as well as the substitution of Li for Ge in the framework should not be disregarded. The maximum Li capacity and the reversibility of the lithiation processes of $\square_{24}\text{Ge}_{136}$ clathrate-II allotropes will need to be studied in future investigations [Böhme2014].

In summary, empty silicon and germanium clathrate-II systems as well as the clathrate-I system $\text{Ba}_x\text{Al}_6\text{Si}_{40}$ have been studied as possible materials for use as anodes in Li-ion batteries. While they showed some positive qualities, such as small volume changes upon lithiation, their mechanisms for Li intercalation are not well understood. Likewise, the reversibility and stability of the lithiated products must be the subject of future investigations.

9. Thermoelectric effects and materials

The advancement of energy conversion technologies that transform heat into electrical energy stand to have a significant impact on our energy-driven world. A phenomenon known as the Seebeck effect is at the heart of thermoelectric based generators, which have the unique ability to convert heat into electrical energy. Initially discovered by *Thomas Seebeck* in 1823, the Seebeck effect is realized as a potential that arises from a material placed in a temperature gradient [Seebeck1823]. Charge carriers excited by the increased temperature diffuse toward the colder, lower energy boundary, generating the electrical potential. Two thermoelectric materials with opposite charge carrier types, held in a temperature gradient and connected in series produce an electrical current [Figure 9.1]. This is the basis for a thermoelectric generator.

Figure 9.1. Schematic of a thermoelectric device.

The opposite effect, known as the Peltier effect, is observed when a current is driven through the system and a temperature gradient is formed [Peltier1834]. These effects had no applications and held little interest beyond simple curiosities for many years, until the 1950's when *Abram Ioffe* demonstrated the immense potential of semiconductors as thermoelectric materials [Ioffe1957]. At the time, semiconductors had not been recognized for their microelectronic capabilities and minimal investigations had been performed. Ioffe proposed they could be used as Peltier coolers in refrigerators. This generated sufficient motivation to spark a wave of semiconductor research, in which many reasonable thermoelectric materials were identified, including Bi_2Te_3 [Satterthwaite1957], PbTe [Goldsmid1955], and SiGe [Dismukes1964]. Ultimately though, these thermoelectric refrigerators were unable to compete with the efficiency and cooling potential of compressor-based coolers.

Today, thermoelectric materials are used in a variety of applications [Bell2008]. Peltier coolers are often implemented in applications where reliability and precise temperature control are required, such as in a CCD (charge coupled device) detectors or in the heat sinks of microprocessors. Likewise, thermoelectric refrigerators are still manufactured, but the efficiencies are insignificant in comparison with modern compressor-based refrigerators [Bansal2011, Zhao2014a]. Thus, much of modern thermoelectric research is directed toward the generation of electrical power through thermoelectric generators. Thermoelectric generators are currently used in space-based applications, namely plutonium-based radioisotope thermoelectric generators (RTG), as RTGs are enticing for extended deep space missions where the effectiveness of photovoltaics may be reduced [Williams2012, Gusev2011].

Alternative and renewable energy sources have become more pertinent in recent years, as questions have been raised regarding future fuel supplies, greenhouse gases, and their impacts on climate change. Thus thermoelectric generators have garnered attention, both as primary power producers [Kraemer2011] and as a secondary waste heat harvester [Bell2008]. However, for this to come to fruition, the energy conversion efficiencies of these generators must be enhanced.

The performance of a thermoelectric generator is dictated by a modified Carnot efficiency (Equation 9.1), dependent on both the temperature differential and on the specific properties intrinsic to the materials making up the generator. A device's energy conversion efficiency, η , can be determined by:

$$\eta = \frac{T_H - T_C}{T_H} \left(\frac{\sqrt{ZT+1}-1}{\sqrt{ZT+1}+\frac{T_C}{T_H}} \right) \quad \text{Equation 9.1}$$

Where, T_H and T_C are the temperatures of hot and cold parts and ZT stands for the dimensionless thermoelectric figure of merit, which is determined by Equation 9.2; where S is the Seebeck coefficient (also known as thermopower), σ is the electrical conductivity, k_{tot} is the total thermal conductivity, and T is the absolute temperature. The thermopower is a measure of the voltage that develops across the material in a temperature gradient ($S = \Delta V / \Delta T$).

$$ZT = \frac{S^2 \sigma T}{k_{tot}} \quad \text{Equation 9.2}$$

The current standard for device materials is a ZT value above 1 [Zhang2016]. Referring to Equation 9.1, while utilizing $ZT = 1$ materials with a $T_H = 373$ K and $T_C = 273$ K, an efficiency of ~5% is observed. When the temperature of the hot region is increased, *i.e.* to $T_H = 773$ K, thus increasing temperature gradient, the thermoelectric efficiency increases up to ~15%. Such efficiency is still insufficient for widespread energy harvesting applications, such as for use in automobile exhaust heat harvesting, where the upper temperatures range from 500 K to 900 K. It is estimated that a device containing materials with ZT values of approximately 3 could achieve the 30% efficiencies ($T_H = 773$ K and $T_C = 273$ K) that are necessary for widespread application. Note that not only is the peak ZT value important, but an average ZT and other related parameters describing material performance over the whole temperature range are also important [Kim2015b]. However, in thermoelectric literature the peak ZT s are often compared and referred to. State-of-the-art materials are advancing toward the goal of a high ZT ; notably nanostructured PbTe, SnSe, and Cu₂Se, with SnSe single crystals reporting a record maximum ZT value of 2.6 [Biswas2012, Zhao2014b, Liu2012a]. Maximizing ZT is crucial for the successful integration of thermoelectrics as an alternative energy producer.

This maximization has proven to be difficult due to the interdependent nature of the properties that ZT depends on. Electrical conductivity, given in Equation 9.3, is proportional to the mobility, μ , charge of the carrier, e , and the charge carrier concentration, n . Furthermore, the relationship between the thermopower and charge carrier concentration can be seen in Equation 9.4, where m^* is the effective mass.

$$\sigma = ne\mu \quad \text{Equation 9.3}$$

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad \text{Equation 9.4}$$

As a result, metals exhibit high electrical conductivities with low thermopowers, while insulators show low electrical conductivities with high thermopowers.

The total thermal conductivity, seen in Equation 9.5, can be expressed by the summation of the electronic and lattice contributions: k_E and k_L , respectively. As the name suggests, k_E is dictated by the electronic structure, and is the result of charge carriers propagating heat. This contribution can be approximated by the Wiedemann-Franz law, Equation 9.6, where L is the Lorenz number [Kim2015c].

$$k_{tot} = k_E + k_L \quad \text{Equation 9.5}$$

$$k_L = L\sigma T \quad \text{Equation 9.6}$$

A schematic dependence of all parameters on the charge carrier concentration is depicted in Figure 9.2. The highest ZT is achieved for heavily-doped semiconductors with a charge carrier concentration ranging from 10^{19} to 10^{21} , depending on the particular system, *i.e.* the mobility and effective mass.

Figure 9.2. Scheme of the isothermal dependences of the ZT (black), Seebeck thermopower (orange), electrical conductivity (blue), total (green) and lattice (dashed green) thermal conductivities on the charge carrier concentration.

9.1. Basic Approaches to thermoelectric materials development

There are two main approaches to the tuning of ZT : i) modification of the electronic structure, *i.e.* charge carrier concentration and mobility, and ii) reduction of the thermal conductivity. Both can be effective methods for tuning thermoelectric materials, and both have certain limitations.

Considering that many of the electronic properties of materials have conflicting trends, and improving one property often worsens another, the electronic contribution to ZT is often gauged by the power factor, $S^2\sigma$. A large power factor indicates that a large voltage and current can be achieved simultaneously. Inspection of the Equations 9.3 and 9.4 shows that the power factor depends on the charge carrier concentration as $\sim n^{-\frac{1}{3}}$, and also depends on the mobility of charge carriers and their effective masses. The optimization of charge carriers is critical to the development of high ZT materials. Most importantly, only one charge carrier type should be present, otherwise opposite carriers will effectively cancel each other out [Snyder2008]. In thermoelectric materials, increasing the carrier concentration tends to lower the thermopower [Heremans2012]. For example, in $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$ Shukang *et al.* showed that the replacement of only 0.2% of Ga with Cu significantly improved the electrical conductivity of this clathrate-VIII, increasing from 189 Scm^{-1} to 309 Scm^{-1} at 300 K for $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$ and $\text{Ba}_8\text{Ga}_{15.97}\text{Cu}_{0.03}\text{Sn}_{30}$, respectively [Deng2011a]. This doping had a detrimental effect on the thermopower, which dropped from $-240 \mu\text{V/K}$ to $-210 \mu\text{V/K}$. Overall, the modifications led to a net enhancement of ZT , which increased from 0.45 to 0.53 at 300 K.

The thermopower can be enhanced by alterations of the density of states near the Fermi level. A steep density of states peak correlates to a flat and narrow band in the band structure, indicative of heavy charge carriers. This can lead to a larger thermopower, though unfortunately this also leads to lower carrier mobility. Band structure engineering can be employed to alter the density of states near the Fermi level by the addition of hybridization gaps, Kondo levels, or resonant levels [Heremans2012, Pei2012]. Resonant levels can be generated by the substitution of elements into a host framework. The overlap of impurity bands, in the density of states, with those of the host's can lead to resonant levels and potentially improve the thermopower [Heremans2008]. Additionally, the impurities are often disordered throughout the bulk material, which can facilitate greater phonon scattering and lower the overall thermal conductivity.

Lowering the thermal conductivity is often achieved by reducing the k_L , the measure of a structure's ability to conduct heat. Strategies for lowering k_L include the use of heavy atoms, size mismatches between neighboring atoms, and disorder caused by dopants or vacancies. Additionally, complex structures with large unit cells inherently exhibit lower thermal conductivities [Toberer2011]. Beyond atomic scale manipulation, nano- and micro-scale structuring can be used to further reduce thermal conductivities by creating boundary layers between the particles within a material [Nolas2006, Sootsman2009, He2013, Biswas2012].

9.2. The Phonon Glass-Electron Crystal concept

Amorphous glasses exhibit low thermal conductivities, nearing the minimum theoretical thermal conductivity of solid materials, attributed to a lack of long-range ordering. In such a system, the conductivity is only limited by a mean free path on the order of interatomic distances. This lack of extended ordering often compromises the material's ability to conduct electrons. Electron crystals, on the other hand, require a highly ordered and extended lattice to conduct their electrons. The phonon glass-electron crystal (PGEC) concept was first introduced by Glen Slack in 1995 [Slack1995]. According to this concept, efficient thermoelectrics will be found among narrow band semiconductors with cage-like structures and inclusion atoms or molecules trapped inside the cages. The rattling of guest atoms will provide effective scattering of the heat carrying phonons thus decreasing the lattice thermal conductivity, k_L , while charge carrier transport will occur through the covalent framework. The thermal and charge transport properties of PGEC phases may be optimized independently to some extent. Two classes of materials fulfill requirements of the PGEC concept, skutterudites and clathrates. For skutterudites with the common formula AM_4E_{12} (A = alkali-, alkali-earth, and rare-earth metal; M = late transition metal; E = P, As, Sb) significant progress was achieved [Sales1996, Leithe-Jasper2003, Li2008, Nolas1999]. In these materials, M and E atoms form a 3D framework containing icosahedral 12-vertex cages. Optimized skutterudite-based TE materials (*e.g.* $CeFe_{4-x}Co_xSb_{12}$ or $Yb_{0.3}Co_4Sb_{12}$) exhibit $ZT > 1.3$ for bulk materials.

Intermetallic clathrates have structures that exhibit PGEC-like properties. The sp^3 covalently bound framework acts as a means to conduct electrons through the structure; while loosely held guest atoms (Figure 9.3) function to scatter phonons and significantly reduce the overall thermal conductivity. The anharmonic motions of loosely bonded guest atoms lead to the reduction of the relaxation times of acoustic phonon modes [Tadano2015]. Due to these motifs, clathrates often have thermal conductivities below 5 W/m-K, while they simultaneously maintain metallic or semiconducting electrical properties. Furthermore, clathrates are viable candidates for band structure engineering, with the potential for adjustable band gaps. This engineering would also allow for an optimization of the power factor with only minimal effects on the thermal conductivity.

Figure 9.3. Rattling of the central atom inside the polyhedral clathrate cage.

10. Trends in the thermoelectric properties of clathrates

Figure 10.1. Absolute values of room temperature Seebeck coefficients (thermopowers) are shown for the majority of studied clathrate systems. Si-based clathrates are shown as squares, Ge-based clathrates are shown as sideways triangles, Sn-based clathrates are stars, cationic clathrates are diamonds, and transition metal-pnicogen (TM-Pn) clathrates are pentagons. The colors of the shapes represent room temperature ZT values. Values increase logarithmically from red (0.00001) to yellow (0.1) to teal (0.7). Any ZT s below 0.00001 are shown as empty shapes. Data sources are given in the Appendix.

Figure 10.2. Room temperature electrical resistivities are shown for the majority of studied clathrate systems. Si-based clathrates are shown as squares, Ge-based clathrates are shown as sideways triangles, Sn-based clathrates are stars, cationic clathrates are diamonds, and transition metal-pnicogen (TM-Pn) clathrates are pentagons. The colors of the shapes represent room temperature ZT values. Values increase logarithmically from red (0.00001) to yellow (0.1) to teal (0.7). Any ZTs below 0.00001 are shown as empty shapes. Data sources are given in the Appendix.

Figure 10.3. Room temperature thermal conductivities are shown for the majority of studied clathrate systems. Si-based clathrates are shown as squares, Ge-based clathrates are shown as sideways triangles, Sn-based clathrates are stars, cationic clathrates are diamonds, and transition metal-pnicogen (TM-Pn) clathrates are pentagons. The colors of the shapes represent room temperature ZT values. Values increase logarithmically from red (0.00001) to yellow (0.1) to teal (0.7). Any ZT s below 0.00001 are shown as empty shapes. Data sources are given in the Appendix.

Figure 10.4. Room temperature lattice thermal conductivities are shown for the majority of studied clathrate systems. Si-based clathrates are shown as squares, Ge-based clathrates are shown as sideways triangles, Sn-based clathrates are stars, cationic clathrates are diamonds, and transition metal-pnicogen (TM-Pn) clathrates are pentagons. The colors of the shapes represent the contribution of the lattice thermal conductivity to the total thermal conductivity, $(\kappa_L/\kappa_{\text{Total}}) \times 100\%$, at room temperature. The lattice thermal conductivity was calculated $\kappa_L = \kappa_{\text{Total}} - \kappa_e$, where the electronic contribution to thermal conductivity was estimated from the Wiedemann–Franz law, $\kappa_e = LT/\rho$. The Lorentz number was estimated using the Seebeck thermopower as $L = (1.5 + e^{-\frac{|S|}{116}}) \times 10^{-8}$ [Kim2015c]. Several cases where deviations from the Wiedemann–Franz law are observed, *i.e.* calculated $\kappa_e > \kappa_{\text{Total}}$, are omitted for clarity. Data sources are given in the Appendix.

While studying the trends of specific systems, it is important to obtain a comprehensive understanding of the properties of the whole class of materials and how these properties vary based on their elemental components. Thus, we present a thorough analysis of the thermoelectric data published for the various inorganic clathrate systems. For this report, we selected papers with properties reported for high density samples, *i.e.* sintered pellet samples with densities over 80% of the theoretical X-ray density and single crystalline samples were included. For samples in which a room temperature ZT value was not

reported, the ZT s were calculated from the published transport properties. In all Figures of this chapter, with the exception of Figures 10.4 and 10.7, the color of the symbol indicates the ZT value at room temperature, with a scale bar provided on the right. Five different symbols are used to differentiate Si-, Ge-, and Sn-based anionic clathrates (squares ■, triangles ▲, and stars ★, respectively), cationic clathrates (diamonds ◆), and tetrel-free transition metal-pnictogen clathrates (pentagons ●). Appendix 1 contains all of the data used to plot the graphs in this chapter.

Thermoelectric properties of clathrates, separated by their elemental compositions, are shown in Figures 10.1-10.4 for absolute Seebeck coefficients, electrical resistivities, as well as for total and lattice thermal conductivities at room temperature. The inverse clathrates $\text{Ge}_{30}\text{P}_{16}\text{Te}_8$, $\text{Ge}_{38}\text{Sb}_8\text{I}_8$, and $\text{Sn}_{38}\text{Sb}_8\text{I}_8$ were cropped from the figure for clarity reasons, since they exhibit the highest absolute values of Seebeck coefficients at $780\text{ }\mu\text{V/K}$, $800\text{ }\mu\text{V/K}$, and $600\text{ }\mu\text{V/K}$, respectively. Sn-based clathrates exhibit the next highest absolute Seebeck thermopower values, up to $390\text{ }\mu\text{V/K}$ for Ba-Cu-Ga-Sn and $370\text{ }\mu\text{V/K}$ for Ba-Ga-Sn. Note that clathrates composed of the same set of elements may have very different Seebeck coefficients, presumably due to the flexible and tunable occupancies of both framework and guest positions resulting in compositional deviations from their ideal charge-balanced composition. For example, the absolute values of Seebeck coefficient (thermopower) in the Ba-Ga-Sn family ranges from 110 to $370\text{ }\mu\text{V/K}$ and changes the sign over the range of stoichiometries, due to the different Ga/Sn ratios.

Considering tetrel-based anionic clathrates, the trend that can be gleaned from Figure 10.1 is that for the majority of clathrates, the absolute Seebeck coefficients increases down the group from Si-, to Ge-, to Sn-based clathrates. This correlates well with the trend in strength of the tetrel-tetrel bond. High values of Seebeck thermopower indicate that the composition of a clathrate phase is close to an electron balanced one. In tetrel-based frameworks such a balance is achieved by either the formation of vacancies or by aliovalent substitution into the tetrel sublattice. Both require the breaking of tetrel-tetrel bonds. This is often achieved for Sn-based clathrates, such as $\text{A}_8[\text{Sn}_{44}\square_2]$ [Kaltzoglou2008c], since the Sn-Sn bond is not particularly strong, $E(\text{Sn-Sn}) = 151\text{ kJ}\cdot\text{mole}^{-1}$ [Mingos1998]. The energy cost of breaking a Si-Si bond, on the other hand, is significantly higher, $226\text{ kJ}\cdot\text{mole}^{-1}$, and for Si-based clathrates, non-electron-balanced compositions are more often the rule rather than the exception. This results in rather low Seebeck thermopower values for most of the Si-based (non-electron-balanced) clathrates, with a few exceptions for which an electron balance was achieved by aliovalent substitutions in the framework. The intermediate strength of the Ge-Ge single bond, $188\text{ kJ}\cdot\text{mole}^{-1}$, has resulted in the largest diversity of Seebeck coefficient values for a Ge-based set of clathrates. Though the number of non-tetrel clathrates is significantly smaller than tetrel-based ones, complete thermoelectric data for five of the systems has been published. In these systems the Seebeck coefficients are consistently small, likely due to their highly metallic natures.

The highest room-temperature ZT values (color-coded) are observed for clathrates with absolute Seebeck coefficients around $250\text{ }\mu\text{V/K}$. However, this data shows that a large Seebeck value does not necessarily indicate a high ZT . Many of the germanides and some of the silicides have large Seebeck coefficients, but show ZT s of lower than 0.1 at room temperature.

Resistivity data shown in Figure 10.2 indicates that high ZT values are achieved for clathrates with resistivities in the range of $0.5\text{-}50\text{ m}\Omega\cdot\text{cm}$. The general trend for these systems is lower values of electrical resistivities at room temperature for Si or Ge-based clathrates than for Sn-based ones. This again correlates with the electron-balanced compositions for most of the Sn-based clathrates that result in lower charge carrier concentrations, and consequently higher resistivities. Tetrel-free clathrates based on transition metals exhibit the lowest resistivities. For the inverse clathrates, very high values of resistivity were reported for $\text{Ge}_{38}\text{Sb}_8\text{I}_8$ and $\text{Sn}_{38}\text{Sb}_8\text{I}_8$. These points are also omitted from the plot for clarity. Many compounds in the $0.5\text{-}50\text{ m}\Omega\cdot\text{cm}$ range still have low ZT s, despite having appropriate electrical resistivities. This shows how dependent ZT is on the combination of all of the thermoelectric properties, and it suggests that one non-ideal property outside of a standard range does not necessarily mean a compound will have poor thermoelectric properties.

Finally, the plot of thermal conductivities (Figures 10.3 and 10.4) is very revealing for clathrates. Not only does it show that all published clathrates have low total thermal conductivities below 6 W/m-K (except Na-Si systems which will be explained later), but the majority of them are below 3 W/m-K. This is good justification that clathrate systems are true PGEC (Phonon Glass-Electron Crystal) systems, with intrinsically low thermal conductivities which are highly independent of their elemental constituents. A comparison of the total and lattice thermal conductivities indicates that electronic contribution plays a minor role for the vast majority of clathrates; data analysis shows that the lattice contribution is above 70% for 3/4 of all clathrate cases (Figure 10.4). Furthermore, the lattice contribution is over 90% of the total thermal conductivity for half of all clathrates. The increase in thermal conductivities for the Na-Si clathrates correlate with an increase in the Na content and accompany the corresponding decrease of the Seebeck thermopowers. This indicates a substantial contribution of the electronic component to thermal conductivity of this metallic-like system [Stefanoski2012].

As expected, the clathrate systems with heavier atoms tend to show lower thermal conductivities. Sn-based clathrates exhibit the lowest thermal conductivities, with the majority of thermal conductivity values at or below 1 W/m-K. This indicates that not only is the rattling of guest atoms important, but so is the contribution of the framework for a reduction in the thermal conductivities. This topic is further considered in Chapter 11. Despite the higher electrical resistivities of the tetrel-free clathrates, they still show thermal conductivities below 5 W/m-K. That of Ba-Au-P shows the lowest thermal conductivity of ~0.6 W/m-K, attributed to the presence of heavy atoms, interface twinning, and anti-phase defects [Fulmer2013]. Overall, the highest figures of merit are seen for the systems with thermal conductivities at or below 1 W/m-K, *i.e.* mainly for the Sn-based clathrates. This data is quite informative, as it shows that, even if the thermal conductivity of a clathrate is unknown and clathrate has an electron-balanced composition (unlike Na-Si compounds), preliminary *ZT*s can be estimated based on the upper limit of thermal conductivity at 4 W/m-K.

Figure 10.5. Room temperature Seebeck coefficients (thermopowers) for *p*-type clathrates (positive Seebeck values) are shown versus room temperature electrical resistivities. Si-based clathrates are shown as squares, Ge-based clathrates are shown as sideways triangles, Sn-based clathrates are stars, cationic clathrates are diamonds, and transition metal-pnicogen (TM-Pn) clathrates are pentagons. The colors of the shapes represent room temperature *ZT* values. Values increase logarithmically from red (0.00001) to yellow (0.1) to teal (0.7). Any *ZT*s below 0.00001 are shown as empty shapes. Data sources are given in the Appendix.

Figure 10.6. Room temperature Seebeck coefficients (thermopowers) for *n*-type clathrates (negative Seebeck values) are shown versus room temperature electrical resistivities. Si-based clathrates are shown as squares, Ge-based clathrates are shown as sideways triangles, Sn-based clathrates are stars, cationic clathrates are diamonds, and transition metal-pnictogen (TM-Pn) clathrates are pentagons. The colors of the shapes represent room temperature *ZT* values. Values increase logarithmically from red (0.00001) to yellow (0.1) to teal (0.7). Any *ZT*s below 0.00001 are shown as empty shapes. Data sources are given in the Appendix.

For thermoelectric devices, two types of legs are required, a *p*-type and an *n*-type. The clathrates' properties can also be broken up into two groups of *n*- and *p*-type materials which also reveal important trends (Figures 10.5 and 10.6). The first noticeable difference is that there are many more properties published for *n*-type clathrates (negative Seebeck coefficients, dominant charge carriers are electrons) than there are for *p*-type clathrates (positive Seebeck coefficients, dominant charge carriers are holes). Another comparison can be drawn between the *ZT*s for both systems. For the *n*-type clathrates, the highest *ZT*s are observed in the systems with electrical resistivities below 10 $\text{m}\Omega\text{-cm}$ and Seebeck coefficients in the range of $-175 \mu\text{V/K}$ to $-300 \mu\text{V/K}$. Alternatively, in the *p*-type clathrates, the highest reported *ZT*s are shifted to higher resistivities and substantially higher Seebeck coefficients. This may be related to the fact that electrons as charge carriers tend to have higher mobilities and lower effective masses than holes. As mentioned in Chapter 9 Equations 9.3 and 9.4, an increase in the mobility of charge carriers, μ , directly

leads to a decrease in the electrical resistivity of a system. Likewise, an increase in the effective masses of carriers directly leads to an increase in the Seebeck thermopower.

Figure 10.7. Room temperature ZT s are shown versus room temperature power factors. Si-based clathrates are shown as squares, Ge-based clathrates are shown as sideways triangles, Sn-based clathrates are stars, cationic clathrates are diamonds, and transition metal-pnicogen (TM-Pn) clathrates are pentagons. The colors of the shapes represent room temperature thermal conductivity values. Values decrease linearly from red (4 W/m-K) to yellow (1.2 W/m-K) to green (0.5 W/m-K). Any thermal conductivities below 0.5 W/m-K are shown as bright green shapes. Likewise, thermal conductivities above 4 W/m-K are shown as dark red shapes. Data sources are given in the Appendix.

Figure 10.8. Room temperature thermal conductivities are shown versus room temperature power factors ($S^2\sigma$). An arrow is drawn to signify the trend in ZT with power factor and thermal conductivity. Si-based clathrates are shown as squares, Ge-based clathrates are shown as sideways triangles, Sn-based clathrates are stars, cationic clathrates are diamonds, and transition metal-pnicogen (TM-Pn) clathrates are pentagons. The colors of the shapes represent room temperature ZT values. Values increase logarithmically from red (0.00001) to yellow (0.1) to teal (0.7). Any ZT s below 0.00001 are shown as empty shapes. Data sources are given in the Appendix.

Figure 10.9. This figure relates room temperature ZT values to their corresponding maximum ZT s. The temperatures at which maximum ZT values are observed is shown for selected elemental systems. The sizes of the shapes correspond to the values of maximum ZT s at the indicated temperatures for the indicated systems. Additionally, the colors of the circles represent the room temperature ZT values. Values increase logarithmically from red (0.00001) to yellow (0.1) to teal (0.7). Any ZT s below 0.00001 are shown as empty shapes. Data sources are given in the Appendix.

Figure 10.7 shows the relationship of ZT to its thermal conductivity, and power factor. The thermal conductivities are shown by color with higher thermal conductivity values in red, and lower thermal conductivity values in green. Gray data represents any data points with either no reported thermal conductivity or a thermal conductivity over 4 W/m-K. High ZT values are achieved for the clathrates which simultaneously maintain a low thermal conductivity and high power factor. The increase in ZT is nearly linear as the power factor increases, which is a nice illustration of the aforementioned trend that the majority of clathrates aside from a few outliers have similarly low thermal conductivities, often below 3 W/m-K. Thus, the impacts of the clathrates' thermal conductivities on the overall ZT values are not only very similar, but they are also far less significant in these systems than the power factors are. This is not the case for many other types of the thermoelectric materials [Rowe1995]. The highest room temperature ZT values ($ZT \sim 0.7$) were reported for Sn-based compounds. An alternative representation of the same trends is shown in Figure 10.8. In this graph, a high power factor correlates with ZT (color-coded in Figure 10.8) due to small variations of the thermal conductivity. Furthermore, while Sn-based clathrates

tend to show the best properties, some silicides and germanides do have high power factors. Though in these cases, their thermal conductivities are higher than the stannides of the same power factors, thus their overall ZT s are reduced.

Figure 10.9 relates the room temperature ZT data to peak ZT data for the separate clathrate systems. The sizes of the bubbles express the sizes of peak temperature ZT s. The trend in the temperatures of maximum ZT s correlates well with the stabilities discussed in Chapter 4. Si clathrates are the most thermally stable system, germanides are less so, and stannides are the least stable clathrates. Peak ZT s are observed at the highest temperatures for Si-based clathrates. Likewise, most germanides and inverse clathrates peak at lower temperatures, and most stannides peak at significantly lower temperatures. Though Sn clathrates have the highest peak ZT values, the maximum ZT temperatures are between 500-550 K. Ge clathrates show maximum ZT s at temperatures between 600-1050 K, and while Si clathrates exhibit lower ZT s than the compounds based on heavier tetrrels, some Si clathrates are stable above 1200 K. In Figure 10.9, the color of the circle corresponds to the ZT value at 300 K. There is a certain correlation between ZT values at room temperature and their peak temperature, *i.e.* most of the large circles have a teal color (high ZT at 300 K and peak temperature). However, this is not true for all clathrates, since several large orange circles (low ZT at 300 K) are present. There are two reasons for such a significant ZT increase: i) ZT is a temperature dependent parameter which is directly proportional to temperature, so for the same values of S , κ and ρ at 300 K and 900 K, the ZT_{900K} is 3 times higher than ZT_{300K} ; ii) all the transport properties, S , κ and ρ are temperature-dependent, and for semiconductors, a strong decrease of resistivity, a slight decrease of thermal conductivity and an increase of Seebeck thermopower is expected upon the increase of temperature above ambient. Figure 10.9 illustrates a necessity for new clathrates containing heavy elements in the framework which are more stable than Sn-based clathrates. Increasing stability of such clathrates up to 1000 K will result in a substantial gain in the thermoelectric figure-of-merit, ZT .

11. Guest Atom Rattling in Clathrates.

Clathrates reliably exhibit low thermal conductivities, thus they have been extensively studied for their use as thermoelectric materials [Iversen2000; Nolas2014; Fulmer2013]. Considerable time and effort have been spent investigating the origins of their intrinsically low thermal conductivities, and this has entailed advanced research methods. Techniques, such as neutron scattering and quantum-mechanical calculations, have been aimed at understanding the guests' contributions to the overall properties of clathrate systems, namely the guests' interactions with their surrounding frameworks. Beginning with the aforementioned phonon-glass electron-crystal description of clathrates, it has been proposed that guest atoms encapsulated in clathrate cages rattle fairly independently of the framework and act as scattering centers. This theory is supported by the large displacement parameters often observed for encapsulated guest atoms. However, this idea has since been contested and the question still remains: how much does the guest actually interact with the framework?

A key to understanding this interaction is through an examination of the vibrational modes in clathrates. Understanding these vibrational states, especially the vibrational states of guest atoms, provides clues to the origin of their low thermal conductivities. Characteristic vibrational frequencies can be calculated from: i) heat capacity measurements; ii) through the analysis of structural parameters obtained from either the single crystal or powder diffraction data; or iii) via the deconvolution of electrical resistivity measurements. Subsequently, these results can be compared to the vibrational modes of observed and calculated phonon spectra.

11.1. Heat Capacity

Experimental heat capacity measurements can be an exceptionally useful tool in understanding the thermal properties of materials. Multiple methods have been established to interpret experimental heat

capacity data. A combined approach, incorporating both Einstein and Debye models, tends to fit the heat capacity data for real clathrate and many clathrate-like systems [Beekman2010b; Sales1999].

The amount of heat energy required to raise the temperature of a material one degree is known as the heat capacity— C_V at constant volume or C_P at constant pressure. When this term is expressed as the amount of heat per unit mass of material needed to raise its temperature by 1 K, it is referred to as specific heat [Fegley2012]. Heat capacity is related to the thermal conductivity of materials, as seen in Equation 11.1, where κ_L is the lattice thermal conductivity, v is the phonon group velocity, and l is the phonon mean free path between scattering points [Nolas2014]. Based on this equation, it is apparent that a higher heat capacity corresponds to a higher lattice thermal conductivity.

$$k_L = \frac{1}{3} C_v v l \quad \text{Equation 11.1}$$

Normal and Umklapp scattering mechanisms are both responsible for heat propagation in extended solids. Through normal scattering, momentum is conserved; in Umklapp scattering, momentum is not conserved. At low temperatures, normal scattering is dominant due to a lower phonon population and Umklapp scattering has just a minor contribution. The converse is often true at higher temperatures, where Umklapp scattering dominates due to increased phonon-phonon scattering. In clathrates, the presence of Einstein oscillators can also lead to Umklapp scattering at low temperatures [Christensen2010].

In the early 1900's, Albert Einstein developed a low-temperature model to predict the heat capacity of solids. This model treats all atoms as independent oscillators with their own unique *Einstein temperatures* (Θ_E), and allows all atoms to freely vibrate in all directions at a single characteristic frequency, ν . The Einstein temperature is related to this characteristic frequency by the equation $\Theta_E = h\nu/k$, where h is Planck's constant and k is Boltzmann's constant. While appropriate in some situations, such as modeling of guest atoms' rattling, it fails to accurately describe the heat capacity trends of extended solids because it neglects interatomic interactions. This is readily apparent at very low temperatures, where the model often diverges from experimental data. Equation 11.2 is the Einstein model for heat capacity, where $u = \Theta_E/T = h\nu/kT$ and R is the gas constant [Fegley2012].

$$C_v = 3R \frac{u^2 e^u}{(e^u - 1)^2} = 3R \frac{\left(\frac{\Theta_E}{T}\right)^2 e^{\left(\frac{\Theta_E}{T}\right)}}{\left(e^{\left(\frac{\Theta_E}{T}\right)} - 1\right)^2} \quad \text{Equation 11.2}$$

Peter Debye later extended Einstein's model to account for the coupling of atomic oscillators seen in real systems. In this model, ν is assumed to be a range of vibrational frequencies, and $\nu_{\max}$ is used in place of ν . Similar to the Einstein model, the Debye model predicts a characteristic *Debye temperature*, Θ_D , which can be determined experimentally. Because Debye's model accounts for atomic interactions, the heat capacities of real systems tend to be better fit using Debye models as opposed to Einstein models. Equation 11.3 is the Debye equation for heat capacity, where $u = h\nu/kT$ and $x = \Theta_D/T = h\nu_{\max}/kT$. The Debye model predicts a $\sim T^3$ temperature dependence of heat capacity, which gives a better fit for the experimental data than the Einstein model does for low-temperature data. The T^3 Debye model can be fit to experimental data for good approximations of the change in heat capacity per temperature [Fegley2012].

$$C_v = 12x^3 \int_0^x \frac{u^3}{(e^u - 1)} du - \frac{3x}{(e^x - 1)} \quad \text{Equation 11.3}$$

Figure 11.1a shows sample experimental heat capacity for the clathrate-I $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$ [data taken from Kovnir2011b]. In a metal, the electronic contribution to the heat capacity can be estimated by plotting very low temperature heat capacity data near 0 K (Figure 11.1b). At these temperatures, the Debye model reduces to Equation 11.4, where γT is an electronic heat capacity, *i.e.* the heat capacity due to the thermal excitation of electrons, while the constant $\times T^3$ portion represents the phonon contribution. A linear fit of C_v/T vs. T^2 yields the Sommerfeld coefficient, γ , as the y-axis intercept. Furthermore, the Sommerfeld

coefficient can be used to predict the density of states at the Fermi level, $N(E_F)$, using Equation 11.5 [Fegley2012].

$$C_v = \frac{1943.8}{(\theta_D)^3} T^3 + \gamma T \quad \text{Equation 11.4}$$

$$\gamma = \frac{\pi^2 k_B^2}{3} N(E_F) \quad \text{Equation 11.5}$$

$$C_{total} = C_{electronic} + C_{Debye} + C_{Einstein\ 1} + C_{Einstein\ 2} + \dots \quad \text{Equation 11.6}$$

Moreover, a plot of C_v/T^3 versus T is useful for determining the presence of Einstein modes [Beekman2010b]. In clathrates, the heat capacity data is best fit by a combination of Debye and Einstein modes, which can be seen as a sum of contributions as in Equation 11.6. Guest atoms in clathrates typically show much larger atomic displacement parameters (ADPs) than their corresponding framework atoms, indicative of weak bonding host-guest interactions and independent Einstein-like oscillations. Conversely, covalent clathrate frameworks often are best described via a Debye model. Figure 11.1c is a pictographic example of the deconvolution of total heat capacity. In the Figure 11.1c, a sample electronic contribution to heat capacity is shown in green, an Einstein oscillator's contribution is shown in orange, and a small Debye contribution is shown in blue near zero.

Figure 11.1. Heat capacity for the clathrate-I $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$: (a) overall temperature dependence; (b) low temperature range (main panel) and whole range (inset) of the C_v/T vs. T^2 dependence used for an estimation of the electronic contribution; (c) C_v/T^3 vs. T dependence used for the estimation of the Einstein contribution. Experimental data are taken from [Kovnir2011b].

11.2. Variable Temperature Diffraction Studies

Vibrational frequencies, and subsequently, characteristic Einstein temperatures obtained from heat capacity fits can be directly compared to those obtained from room temperature single crystal data. However, such estimations from crystal data are highly dependent on the quality of the data collected, and are subject to instrumental systematic errors as well as refinement errors [Sales1999; Johnsen2010].

If single crystal data for a material is collected at multiple temperatures, or if systematic Rietveld refinements are performed for a polycrystalline material at multiple temperatures, one can observe a temperature dependence of the atomic displacement parameters. Utilizing Equation 11.7, the isotropic ADPs, U_{ISO} , of rattling atoms can be used to estimate the characteristic Einstein temperatures or rattling frequencies of guest atoms. In this equation, m is the mass of the oscillating atom, d^2 is a characteristic temperature-independent disorder, and once again $\Theta_E = \hbar v/k$ [Fegley2012; Sales1999].

$$U_{ISO} = \frac{\hbar^2}{2mk_B\Theta_E} \coth \frac{\Theta_E}{2T} + d^2 \quad \text{Equation 11.7}$$

As clathrate guests' displacements tend to be quite anisotropic, each special position can have multiple vibrational modes corresponding to different directions of motion. For clathrate-I, the rattling of the guest atoms in the larger tetrakaidecahedra can be described using two main directions, parallel to the large hexagonal face of the tetrakaidecahedra and perpendicular to it. Correspondingly, two Einstein temperatures, Θ_{E11} and Θ_{E22} , are often reported, which are calculated from substituting U_{11} or U_{22} into Equation 11.7, respectively [Johnsen2010; Mano2011].

11.3. Phonon Calculations

Phonon dispersion curves show phonon propagation between chosen directions in the reduced reciprocal unit cell. Flat bands indicate slower group velocities and therefore a higher possibility for lower thermal conductivities using **Equation 11.1** [Christensen2010]. Due to the high computational costs associated with phonon calculations along with the difficulties encountered when calculating phonon spectra for complex compounds, crystal structures are typically simplified by removing mixed sites and other disorder in the structures.

In 2001, *Dong et al.* introduced strong evidence that guest atoms play an important role in the overall thermal properties of clathrates. In their study of Ge systems, an order of magnitude decrease in the thermal conductivity was calculated when going from a supercell of a simple diamond Ge structure, to a supercell of an empty type-I clathrate, Ge_{46} , with a much larger unit cell [Dong2001]. Moreover, the introduction of a guest atom into the cages of Ge_{46} led to a further decrease in the thermal conductivity by a second order of magnitude. The first drop in thermal conductivity from diamond *d*-Ge to Ge_{46} can easily be related to the vast increase in the complexity of the structure, *i.e.* an increase in the number of atoms per unit cell and unit cell volume. As can be seen from their phonon dispersions, these factors directly influence the number of phonon modes in each system along with their sharpness/flatness, increasing the probability of phonon scattering and decreasing group velocities. In contrast, despite the large drop in thermal conductivity between the phases, the calculated phonon dispersions for Ge_{46} and the theoretical filled $\text{Sr}_8\text{Ge}_{46}$ show much fewer differences in their dispersions and in the number of phonon modes present.

The most significant contribution of Sr to the dispersion of $\text{Sr}_8\text{Ge}_{46}$ arises at the low energy range of the spectrum. The introduction of Sr optical phonon modes into the Ge framework causes an “avoided crossing” of the host framework’s acoustic modes. This avoided crossing has been calculated and experimentally observed for a range of clathrate structures [Christensen2010; Nolas2014]. Expanding upon this further, Ge_{46} has three acoustic phonon modes (modes starting from zero at Γ point) that dominated the low energy range of the spectrum from 0 cm^{-1} to approximately 80 cm^{-1} . These long modes have large slopes, corresponding to large group velocities, which in turn lead to large thermal conductivities. With energies near those of the original acoustic modes, the Sr optical phonon modes interrupt the propagation of the acoustic modes, creating an avoided crossing. The Sr guests not only introduce new phonon modes into the material, but they also cause the acoustic host framework modes to flatten. This flattening decreases their group velocities and lowers the overall thermal conductivity of the material.

Figure 11.2 shows an example of phonon dispersion curve for an induced avoided crossing by the introduction of a low energy guest mode (center). Before the guest (green line) is introduced, the acoustic phonon modes have large group velocities, and they propagate to high energies. Upon the introduction of the guest mode, the acoustic modes are diverted and their group velocities (heights) decrease.

Figure 11.2. A schematic low energy partial phonon dispersion for: a clathrate framework (left), alongside a schematic of an avoided crossing (middle), and a partially avoided crossing (right). Framework phonons are shown in blue (acoustic) and orange (optical) and guest phonon mode is shown in green.

This avoided crossing can play a pivotal role in the overall thermal conductivity in extended solids. Acoustic phonon modes (blue in Figure 11.2) start from zero at the Γ point, and often have large effects on the heat propagation in solids, since they tend to have large group velocities and long wavelengths. Optical phonon modes (orange in Figure 11.2) have lower group velocities and shorter wavelengths [Christensen2010; Nolas2014]. The overlap of optical and acoustic branches is a common mechanism for heat scattering. The introduction of rattling guest atoms into the centers of the polyhedral cages of clathrates results in the generation of lower energy optical phonon bands (green in Figure 11.2) which appear near the bottom of a phonon dispersion diagram due to their larger wavelength and lower frequency vibrations. The presence of these newly-generated low energy guest phonon bands near the host acoustic modes interrupts the acoustic phonons' propagation, shortening their wavelengths, and decreasing their group velocities, thus resulting in lower thermal conductivity.

11.4. Resistivity

The temperature dependence of electrical resistivities for metals can also be used to extract Debye temperatures using an extended Bloch-Grüneisen law, or Bloch-Grüneisen-Einstein fit, Equation 11.8. Further information on this topic can be found elsewhere [Kittel2004]. As an example, by using the Einstein temperatures calculated from atomic displacement parameters, *Zeiringer et al.* showed the applicability of Equation 11.8 for estimation of the electrical resistivity of the metallic clathrate $\text{Sr}_8\text{Cu}_{5.3}\text{Ge}_{40.7}$. In this case, the extracted Debye temperature, 193 K, was lower than the values obtained from ADPs and heat capacity: 268 K and 258 K, respectively [Zeiringer2014].

$$\rho_{el}(T) = \rho_0 + 4A \left(\frac{T}{\theta_D} \right)^5 \int_0^{\frac{\theta_D}{T}} \left[\frac{x^5}{(e^x - 1)(1 - e^{-x})} dx \right] + B \{ \theta_{E11} - \theta_{E22} + T \ln \left(\frac{e^{\frac{\theta_{E22}}{T}} - 1}{e^{\frac{\theta_{E11}}{T}} - 1} \right) \} \quad \text{Equation 11.8}$$

11.5. Inelastic Neutron Scattering.

Experimental examinations of phonon vibrational modes can be done in a variety of ways, often including Raman spectroscopy, or the less readily available, inelastic X-ray and neutron scattering (IXS and INS). Neutron scattering provides a few key advantages over other phonon probing methods. For instance,

thermal neutrons are in the same energy and momentum vector ranges as phonons, and they can therefore be used to not only study atomic structure, but also to study structural dynamics. Additionally, neutrons can interact with both light and heavy atoms equally well. The extent of this interaction is not electron density-dependent, but is instead element- and isotope-dependent [Delaire2011]. Thus, neutron scattering can be used to probe the origins and subtleties of experimental thermal conductivities, as was done for the ultralow thermal conductivity material SnSe [Li2015a].

While direct relationships between experimental inelastic neutron scattering spectra and calculated vibrational frequencies are complex, it is straightforward to present calculated phonon density of states spectra broken up by their elemental components. In this way, each element's contributions to the overall spectra can be determined. If the calculation matches the experimental data well, Gaussian fits can be applied to the main peaks in the calculated spectra for the guest atoms and Einstein temperatures can be extracted. *Johnsen et al.* evaluated the Einstein temperatures Θ_{E11} and Θ_{E22} for the clathrate series $\text{Ba}_8\text{M}_6\text{Ge}_{40}$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) using multiple methods including INS, and they showed how significantly the Einstein and Debye temperatures can vary between methods. In these cases, $\text{Ba}_8\text{Au}_6\text{Ge}_{40}$ has the best agreement between INS and single crystal ADPs dependence with 72.6(4) K and 57.5(2) K for Θ_{E11} and Θ_{E22} , respectively, for INS and 84(1) K and 62(1) K, respectively, for ADPs [Johnsen2010].

11.6. Summary of reported experimental data

Overall, a variety of methods can be used to calculate Einstein and Debye temperatures, *i.e.* the characteristic guest vibrational frequencies of clathrates, though one may not be as easily accessible as the other. A summary of data for Debye and Einstein temperatures for clathrates published prior to 2014 can be seen in the very comprehensive tables compounded by *Falmbigl et al.* [Nolas2014]. Table 11.1 summarizes some of the recently published data. Debye and Einstein temperatures calculated from X-ray ADP dependencies and heat capacity (HC) data are presented along with a few exceptions denoted at the base of the table. Though most of the published Debye and Einstein temperature data are for clathrate-I systems, some data also exists for clathrate-II, clathrate-VIII, and clathrate-IX compounds.

As mentioned previously, since the guest atoms in clathrates generate lower energy phonon bands than the framework atoms, they experience low frequency vibrations. Because of this, their characteristic Einstein temperatures are much lower than their respective Debye counterparts. The cationic clathrate systems are no exception as can be seen for the clathrate-I $[\text{Si}, \text{P}]_{46}\text{Te}_{6.8}\text{Se}_{1.2}$. In this system, Te and Se atoms are the guest atoms sitting in the centers of the Si-P clathrate polyhedra, and they indeed have larger ADPs than the framework atoms. Thus, the temperature dependence of their ADPs is more pronounced. The calculated Debye temperature, 491 K, for this system is large and corresponds to a high frequency vibration, which can be related to its elemental components [Abramchuk2012]. Similar large Debye temperatures are observed in other Si systems, such as: $\text{Ba}_8\text{Ga}_{16}\text{Si}_{30}$ and $\text{Ba}_8\text{Cu}_5\text{Si}_x\text{Ge}_{41-x}$, with Debye temperatures of 416 K and 420 K, respectively (Figure 11.3). Interestingly, $[\text{Si}, \text{P}]_{46}\text{Te}_{6.8}\text{Se}_{1.2}$ exhibits very large calculated Einstein temperatures, 153 K and 108 K [Abramchuk2012]. Those values are among the largest reported isotropic Einstein temperatures [Nolas2014].

Figures 11.3-11.6 summarize the representative data for the clathrate-I compounds based on Si, Ge, and Sn. As seen in Figure 11.3, Debye temperatures for silicides (with an average atomic mass per atom ranging from 27.3-63.4 amu) are the highest. Germanides' (63.5-94.7 amu) Debye temperatures tend to be slightly lower, and stannides (94.7-121 amu) have the lowest Debye temperatures. Only Debye and Einstein data from heat capacity measurements and diffraction experiments are shown in the Figures 11.3-11.6. The data from other methods were more scarce and scattered. From an analysis of the reported Debye and Einstein data, it is obvious that each measurement method can present very different results, even for the same system, and data analysis is to some extent subjective. Using $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ as an example, eight papers have presented calculated Debye and Einstein temperatures for this system. Heat capacity analyses of the Debye temperature range from 288 K to 355 K. Similarly, diffraction data

analyses have resulted in a Debye temperature range from 275 K to 312 K. Thus, the data from these two methods vary within a range of 80 K. Einstein temperature data for this system also varies with the minimum Einstein modes calculated from heat capacity ranging from 38 to 80 K [Nolas2014]. It should be noted that a small Ga/Ge non-stoichiometry (see Chapter 7.1) may be responsible for the variation in Debye and Einstein temperatures.

Figure 11.3. The relationships between Debye temperatures and average atomic weights per atom of the clathrates. Most of the data were obtained from [Nolas2014], while references for the rest can be found in Table 11.1.

Figure 11.4. The relationships between Debye temperatures and average atomic weights per atom with respect to clathrates' thermal conductivity. Most of the data were obtained from [Nolas2014], while references for the rest can be found in Table 11.1.

A clear trend can be seen in Figure 11.4, where the Debye temperatures are presented, with thermal conductivity shown by color. Red is the highest thermal conductivity and blue is the lowest. This trend shows that clathrates with lower Debye temperatures and higher average atomic masses tend to have lower thermal conductivities. This correlates well with the trends observed for the thermal conductivity of clathrates discussed in the previous section.

The data for Einstein temperatures is shown in Figure 11.5. The top panel of this figure shows the data extracted from the heat capacity experiments and diffraction experiments with Einstein modes calculated isotropically. The bottom panel of the Figure 11.5 shows diffraction data that was presented anisotropically for the guest atoms in the large cage. No obvious trends are observed in Figure 11.5. One can speculate that the Einstein temperature decreases with an increase in the average atomic mass per atom, but this tendency is weak and not as pronounced as the trend for Debye temperatures. For anisotropic Einstein temperatures, for the guest $6d$ position in clathrates-I with $Pm\bar{3}n$ symmetry, $U_{22} > U_{11} = U_{33}$. Einstein temperatures calculated from U_{22} for the large cage have the lowest values, while Einstein temperatures calculated from U_{11} are higher, and the Einstein temperatures calculated from isotropic motion of the guest atoms in the small cages have the largest values, comparatively. Analysis of the reported Einstein temperatures of clathrates illustrates that their thermal properties cannot merely be described by using a simple rattling model in which a decrease in the thermal conductivity is only directly related to an increase in the guest atoms' weights. The rattling, and, correspondingly, the thermal conductivity, depends on both the relative sizes of the guest atoms and on the inner volumes of the cages available to the rattlers.

Figure 11.5. Top: Isotropic Einstein temperatures deduced from heat capacity and diffraction data; Bottom: Anisotropic Einstein temperatures from diffraction data for U_{11} and U_{22} of the large cages, and those of the small cages. Most of the data were obtained from [Nolas2014], while references for the rest can be found in Table 11.1.

Selected examples of the Einstein temperatures for three clathrate families are shown in Figure 11.6. In the case of $\text{Sr}_8\text{Ga}_{16}\text{Si}_x\text{Ge}_{30-x}$, there is an obvious decrease in the Einstein temperature as the Ge content and the volume of the cages increases [Suekuni2007]. For the Ge-free compound, the Einstein temperature is approximately 90 K, and it decreases to approximately 62 K for the Si-free counterpart. A second trend can be seen in the Einstein temperatures for the out-of-plane motion of Ba in the large cages of the $\text{Ba}_8\text{Au}_x\text{Si}_{46-x}$ clathrate-I system [Aydemir2011]. As the Au content increases from $x = 4.1$ to 5.6, the Einstein temperature decreases, but from $x = 5.6$ to $x = 6.1$, the Einstein temperature increases. This can be partially explained by the size of the cages. The lattice parameters of both $x = 5.6$ and $x = 6.1$ phases are nearly equal, but the addition of more Au atoms into the framework likely decreases the available space for guests inside the cage, leading to a higher Einstein temperature for the Au-rich phase [Zhang2011]. A linear dependence of the Einstein temperature versus “free” cage space in tetrel Ba clathrates has been observed, which suggested less cage space leads to higher Einstein temperatures [Nolas2014]. Moreover, chemical bonding between Au and Ba was recently detected in the $\text{Ba}_8\text{Au}_{5.3}\text{Ge}_{40.7}$ clathrate, indicating that, in compounds with high Au content, the rattling of Ba atoms may be additionally limited by bonding with the framework [Zhang2011].

Figure 11.6. Trends in Einstein temperatures for selected clathrate systems. U_{11} and U_{22} data were averaged to obtain the plots of average Einstein temperature [Suekuni2007, Xu2012, Aydemir2011].

Table 11.1. Debye and Einstein temperatures for selected clathrates. A comprehensive overview for most of the other clathrates is provided by *Falmbigl et al.* [Nolas2014].

Structure	Θ_D (ADP) (K)	Θ_D (H _C) (K)	Θ_E (ADP) (K)	Θ_E (H _C) (K)	Reference
$\text{K}_{6.71}\text{Au}_{2.28}\text{Ge}_{43.72}$	—	280	—	—	[Zhang2013]

$\text{Ba}_8\text{Cu}_5\text{Si}_x\text{Ge}_{41-x}$	420	—	—	—	[Yan2013]
$\text{Sr}_8\text{Cu}_{5.3}\text{Ge}_{40.7}$	268	258	68, 76	42, 75	[Zeiringer2014]
$\text{Ba}_8\text{Ni}_{4.1}\text{Ge}_{41.9-y}\square_y$	—	305	—	70, 75	[Aydemir2015]
$\text{Ba}_{4.9}\text{Sr}_{3.1}\text{Cu}_{5.4}\text{Ge}_{40.6}$	276	—	67, 93	—	[Zeiringer2014]
$\text{Ba}_8\text{Au}_{5.3}\text{Ge}_{40.7}$	—	270	—	—	[Zhang2013], [Zhang2011]
$\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$	—	312	—	33, 80	[Xu2011], [Bentien2005]
$\text{Ba}_8\text{Cu}_{5.1}\text{Ge}_{40.2}\text{Sn}_{0.7}$	230	270	60, 97	60, 80	[Xu2015]
$^*\text{Cs}_8\text{Na}_{9.9}\text{Tl}_{6.1}\text{Ge}_{136}$	—	217	—	56.9	[Zhang2015]
$[\text{Si}, \text{P}]_{46}\text{Te}_{6.8}\text{Se}_{1.2}$	491	—	108, 153	—	[Abramchuk2012]
$\text{Sn}_{24}\text{P}_{19.3}\text{Br}_x\text{I}_{8-x}$	—	220	—	—	[Kovnir2004c]

* Clathrate-II

12. Future Directions of Clathrate Research

In this review, we have shown that inorganic clathrates are a diverse class of compounds with unique properties as well as rich compositional and structural chemistries. Complex relationships between the structural, electronic, and phononic properties of clathrates give rise to a variety of useful properties, such as tunable band-gaps and charge carrier concentrations, superconductivity, high Li-ion mobility and storage capacity, and ultralow thermal conductivities. There are few, if any, classes of the inorganic extended solids, which combine all of the aforementioned properties. Among the many possible applications of inorganic clathrates, their thermoelectric applications currently prevail. A detailed analysis of most of the data published over several decades demonstrated that high thermoelectric figures of merit can be realized in clathrate materials. The vast majority of clathrates exhibit low thermal conductivities—a highly desirable trait for efficient thermoelectric materials. For the tetrel-based clathrates, a clear trend is observed: the highest thermoelectric efficiencies are observed for Sn-based clathrates, which exhibit the lowest thermal stabilities. On the other hand, thermally stable Si-based clathrates often exhibit only moderate efficiencies. This allows us to outline a few possible directions for the future clathrate thermoelectrics research. One suggested route for achieving a combination of high thermal stability with high thermoelectric efficiency is to develop clathrates with mixed Si-Sn frameworks. The advantages of a mixed Si-Sn anionic sublattice were demonstrated for the non-clathrate compound $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$, which has a superior thermoelectric efficiency ($ZT \sim 1.1$ at $\sim 800\text{K}$) to that of the plain Mg_2Si , and maintains a high thermal stability up to 870 K [Zaitsev2006, Liu2012b, Zhang2008]. The “dilution” of a Sn clathrate framework with Si will eliminate the weak Sn-Sn bonds in the framework, while maintaining the low thermal conductivity typical for clathrates composed of heavy atoms. Another viable option is to search for more polar frameworks, such as those found in the tetrel-free clathrates. For example, transition metal-phosphides exhibit significantly higher thermal and chemical stabilities than Sn-based clathrates. This relatively new and small subgroup of clathrates was shown to exhibit rich structural chemistries and extremely low thermal conductivities, while the charge transport properties can be further modified by proper aliovalent substitutions. The thermoelectric potential of the tetrel-free clathrates is still underexplored.

An optimization of the power factor for clathrate-based thermoelectrics can be guided by simple electron counting using the Zintl approach. The prediction of temperature-dependent charge transport properties is still an expensive computational task for highly complex systems with 50-200 atoms in the unit cell. However, the development of computational methods and advancements in computing capabilities should allow for easier predictions of the stabilities and structures of clathrate compositions, along with predictions of their thermoelectric performances [He2014b, Cerqueira2016]. In such a case, a combined experimental and computational screening will facilitate the discovery of novel and efficient thermoelectric materials based on clathrates. The hitherto accumulated expertise in the synthesis and properties characterization of selected clathrate compositions will play a crucial role in any further developments of clathrate-based thermoelectric materials.

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