

Chapter 2

Solid State Chemistry of Clathrate Phases: Crystal Structure, Chemical Bonding and Preparation Routes

Michael Baitinger, Bodo Böhme, Alim Ormeci and Yuri Grin

Abstract Clathrates represent a family of inorganic materials called cage compounds. The key feature of their crystal structures is a three-dimensional (host) framework bearing large cavities (cages) with 20–28 vertices. These polyhedral cages bear—as a rule—guest species. Depending on the formal charge of the framework, clathrates are grouped in anionic, cationic and neutral. While the bonding in the framework is of (polar) covalent nature, the guest-host interaction can be ionic, covalent or even van-der Waals, depending on the chemical composition of the clathrates. The chemical composition and structural features of the cationic clathrates can be described by the enhanced Zintl concept, whereas the composition of the anionic clathrates deviates often from the Zintl counts, indicating additional atomic interactions in comparison with the ionic-covalent Zintl model. These interactions can be visualized and studied by applying modern quantum chemical approaches such as electron localizability.

2.1 Clathrates as Cage Materials: From Minerals to Intermetallic Compounds

Clathrates belong to a large group of inorganic materials called cage compounds. The crystal structures of these substances are built of three-dimensional host frameworks with embedded guest species within large cavities (cages) of the framework. Representatives of this group are found among different families of inorganic materials—from silicate minerals to intermetallic compounds. In particular, minerals of the zeolite family are known for their ability to bear other

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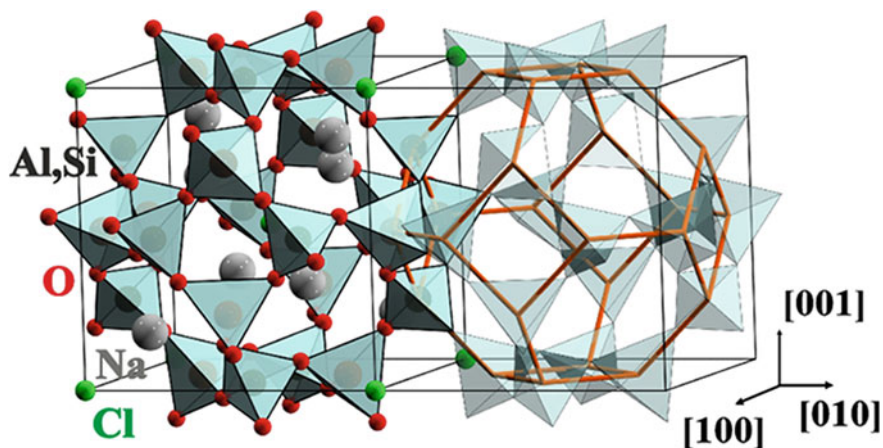


Fig. 2.1 Crystal structure of the mineral sodalite $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2$ (left) with a structural pattern of the clathrate-VII type visualized by the *brown* graph (right)

substances, e.g. smaller molecules such as CH_4 or CO_2 , in the cavities of their crystal structures [1]. As an example, the crystal structure of the mineral sodalite $\text{Na}_4[\text{Al}_3\text{Si}_3\text{O}_{12}]\text{Cl}$ [2, 3] constitutes one of the prototype atomic arrangements for cage compounds, the so-called clathrate-VII pattern [4, 5]. Its framework is formed by $[\text{SiO}_4]$ and/or $[\text{AlO}_4]$ tetrahedral units sharing oxygen vertices of neighboring tetrahedrons (Fig. 2.1). The formal charge of these units can be calculated from the structural formulas as $[\text{SiO}_{4/2}]^0$ and $[\text{AlO}_{4/2}]^{1-}$, where the subscript denominator denotes the number of tetrahedrons between which the given atom is shared. Because of the difference in electronegativity between silicon or aluminum on the one hand and oxygen on the other hand, the Si–O and Al–O bonds are covalent polar. The resulting three-dimensional framework carries negative charge. It comprises tetrakaidecahedral $[4^6 6^8]$ cavities which are filled by $[\text{ClNa}_4]^{3+}$ units, so that charge compensation is achieved according to $(\text{Na}^{1+})_8[(\text{AlO}_{4/2})^{1-}]_6[(\text{SiO}_{4/2})^0]_6(\text{Cl}^{1-})_2 = \text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2$.

A similar spatial organization is observed in the clathrate hydrates, the oldest known group of clathrate compounds. The formation of such substances was already reported by Davy [6] and Faraday [7]. The crystal structures were solved more than a 100 years later [8–13]. The prototype clathrate hydrates have been named by roman numbers or letters. In the clathrate-I crystal structure with ideal composition $X_8(\text{H}_2\text{O})_{46}$ (X stands for a small molecule), the framework is built of water molecules connected via hydrogen bonds (Fig. 2.2, left). The covalent- and hydrogen-bonded O–H–O groups are arranged in such a way that pentagondodecahedral and tetrakaidecahedral cages are formed. The whole network can be described as being formed by neutral $[\text{OH}_{4/2}]$ groups. It is therefore uncharged and the cavities can bear neutral molecules of appropriate size according to the balance $(X^0)_8[(\text{OH}_{4/2})^0]_{46} = X_8(\text{H}_2\text{O})_{46}$. Hence this clathrate family is referred to as

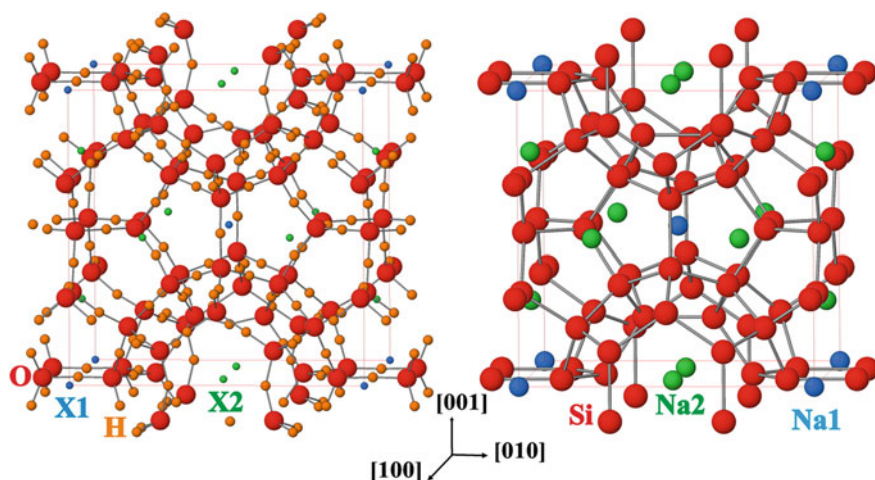


Fig. 2.2 Relationship between the clathrate-I-type crystal structures of the clathrate hydrates ($X_8(H_2O)_{46}$, *left*) and the intermetallic clathrates (Na_8Si_{46} , *right*)

neutral from a chemical point of view. The framework of the mineral melanophlogite $X'_6X''_2(SiO_2)_{46}$ can be derived by substitution of $[OH_{4/2}]$ in the clathrate-I-type structure by $[SiO_{4/2}]$ units [14]. Melanophlogite is a silica modification belonging to the clathrasil family [15, 16]. In clathrasils, the framework is stabilized by covalent Si–O bonds. Unlike the aforementioned sodalite containing $[AlO_{4/2}]^-$ units, the framework in clathrasils carries no charge. As is the case for clathrate hydrates, the cavities therefore can host neutral molecules.

Formally, removing the hydrogen atoms from the clathrate hydrate structure and forming direct bonds between the tetrahedron centers yields the structural motif of intermetallic clathrates. This way (Fig. 2.2), the crystal structure of $X_8(H_2O)_{46}$ may be transformed into that of Na_8Si_{46} [17]. In this case, the framework carries negative charge so that this type of clathrate is referred to as anionic. Consequently, the guest atoms are positively charged. From the crystallographic point of view the same type of crystal structure describes the so-called inverse clathrates, e.g. $Ge_{38}P_8I_8$ [18], with inverse polarity of guest and host substructure, i.e. guest iodine as anion. Despite the formal crystallographic difference in the number of atoms in the unit cell and their chemical functionality, all four crystal structures are considered to belong to the clathrate-I type. The notation originates from work on hydrate clathrates and has been adopted for the other clathrate families [4, 5].

This chapter deals with the chemical composition, crystal structures and their crystallographic features, chemical bonding and preparation routes of intermetallic clathrates.

2.2 Crystal Structures: From Polyhedron Packing and Chemical Composition to Substitutional and Positional Disorder

2.2.1 Polyhedral Cages and Their Packings

Intermetallic clathrates attract the attention of many research communities because of their favorable physical behaviors, e.g. as promising thermoelectric materials. The structural characteristics of this family have recently been summarized in extended reviews [19–23]. One of the key structural features of intermetallic clathrates are frameworks formed predominantly by four-connected atoms. The densest framework of this kind is the well-known crystal structure of diamond. This is in particular because of the staggered conformation of all neighboring atoms. In clathrate structures the neighboring framework atoms in the eclipsed conformation are also present. This local arrangement leads to a less dense framework with differently sized cavities (polyhedral cages) therein. The cavities found in intermetallic clathrates have most commonly the shape of 20-atom dodecahedron, but also the less-observed larger polyhedrons like 24-atom tetrakaidecahedron, 26-atom pentakaidecahedron and 28-atom hexakaidecahedron (Fig. 2.3). In the crystal structures of clathrates I, II, III, IV and V, only these four basic polyhedral cages occur; the space of the structures thus formed is filled completely by arranging the polyhedrons appropriately.

The host framework may be modified either by changing the ratio of staggered and eclipsed host atoms (at least by occurring of the framework atoms in an intermediate conformation) or by introducing three-bonded atoms. In both cases, the consequence is the formation of additional cavities of different size. In this way, in the crystal structure of the clathrate-VIII type, $(20 + 3)$ polyhedrons (derived from the dodecahedron) are condensed so that additional small eight-vertices empty cavities appear [24]. The crystal structure of $\text{Ba}_6\text{In}_4\text{Ge}_{21}$ (clathrate *cP124* or type IX) is characterized by a chiral framework of condensed dodecahedrons. The channels within this framework constitute the so-called *Y* graph. The structure represents an intermediate between clathrates and zeolites [25]. The space within this framework is filled by larger irregular 20-atom polyhedrons, filled e.g. by barium atoms in $\text{Ba}_6\text{Ge}_{25}$ [26–28]. In addition, smaller 11-vertices cavities formed mainly by three-bonded germanium atoms appear which are partially filled by potassium atoms in $\text{K}_{6+x}\text{Sn}_{25}$ [29].

The crystal structure of recently discovered BaGe_5 (clathrate *oP60*) [30] is formed by Ba-centered Ge_{20} dodecahedrons arranged on an orthorhombic lattice and interconnected via three-bonded germanium species to two-dimensional layers. Between the layers, Ge_{24} polyhedrons and additional smaller cavities are formed, which host the remaining Ba atoms, in analogy to $\text{Ba}_6\text{Ge}_{25}$.

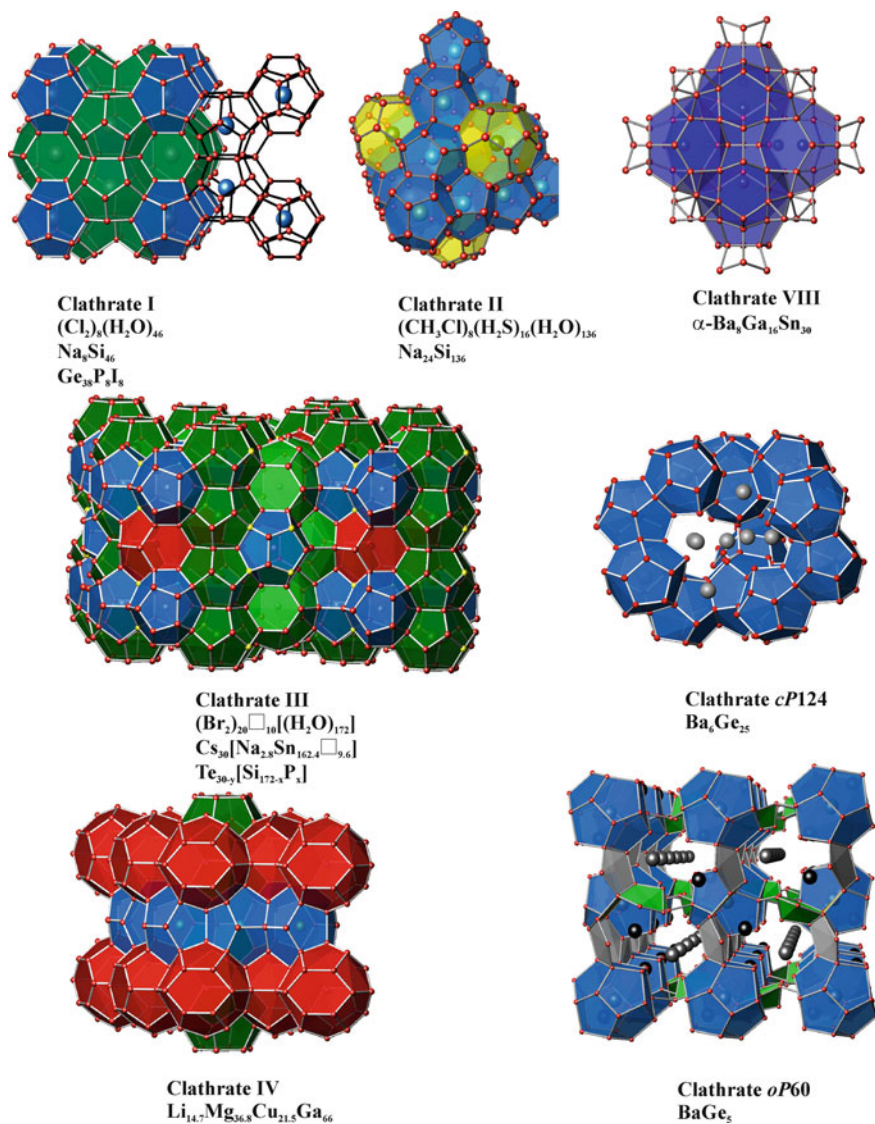
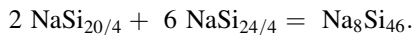


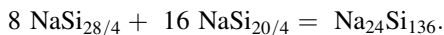
Fig. 2.3 Crystal structures of intermetallic clathrates represented as packing of cage polyhedrons: 20-atom dodecahedron (*blue*), 24-atom tetrakaidecahedron (*green*), 26-atom pentakaidcahedron (*red*) and 28-atom hexakaidecahedron (*yellow*). The example compositions for different clathrate families (hydrate, cationic, and anionic) are given for comparison

2.2.2 Chemical Composition

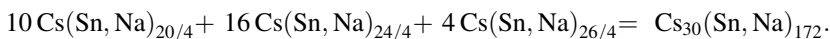
The composition of clathrates with crystal structures built-up of space-filling polyhedrons (e.g. clathrates I, II, III and IV) can be calculated using the formalism mentioned above for the sodalite type of structure. For these clathrates, the composition results from the fact that each framework atom is shared by four polyhedral cages. For the first observed intermetallic clathrate I, $\text{Na}_8\text{Si}_{46}$ [17, 31–33] with two NaSi_{20} and six NaSi_{24} polyhedrons in the unit cell, the content of the unit cell is



For the clathrate II with partially filled cavities, $\text{Na}_{24-x}\text{Si}_{136}$ [17, 31–35], the ideal composition can be obtained from the following balance:



For the clathrate III $\text{Cs}_{30}(\text{Na}_{2.5}\text{Sn}_{162.6}\square_{6.9})$ [36], in fact with defects in the framework, the idealized content of the unit cell (without defects) can be calculated as



For the clathrates VIII, *cP124* and *oP60*, which do not consist of space-filling centered polyhedra, the correct composition of the unit cell can be obtained by taking into account also the empty cavities and atoms contributing to more than four cages.

2.2.3 Crystallographic Disorder and Complexity of the Crystal Structures of Clathrates

Despite very clear structural motifs based on four-connected atoms within the frameworks, the clathrates seldom have completely ordered crystal structures. Different kinds of crystallographic disorder appear including defects in the framework and in the cages, mixed occupation by different elements, and positional disorder of the so-formed sub-sites. The resulting defect or substitution variants tend to form superstructures by ordering of defects or different atoms on the substitution positions. Most of these effects have already been studied on representatives of the clathrate-I type, thus some such examples are given below.

In the structural pattern of the clathrate-I type, the framework is formed by three positions called hereafter as position 1 (Wyckoff site $6c$, $\frac{1}{4} 0 \frac{1}{2}$), 2 (Wyckoff site $16i$, xxx , $x \approx 0.18$) and 3 (space group $Pm\bar{3}n$, Wyckoff site $24k$, $0yz$, $y \approx 0.30$, $z \approx 0.11$). The interatomic distances are usually close to the sum of the covalent radii of the constituting atoms. The average distance between the

framework atoms increases slightly with the size of the cation, e.g. $d(\text{Si-Si})$ changes from 2.37 Å for $\text{Na}_8\text{Si}_{46}$ to 2.42 Å for $\text{Cs}_{8-x}\text{Si}_{46}$ [37]. Position 2 is participating in the five-ring faces of the adjacent polyhedral cages only, i.e. it is a crossing point of six pentagonal faces. All bond angles here are close to the tetrahedral one. Position 3 is located at the crossing point of five pentagonal and one hexagonal face, having one angle within the hexagon which tends to be much larger than the tetrahedral one. Position 1 is located at the crossing point of two perpendicular six-ring faces and four five-ring faces of adjacent tetrakaidecahedrons. It has two angles tending to exceed the tetrahedral one. The deviation of the bond angles from the tetrahedral value also depends on the size ratio of host and guest atoms. With increasing guest-to-host ratio the angles approach the tetrahedral value at positions 2 and 3. For position 1 the trend is opposite (Table 2.1): for the same anion (Si) the deviation from the tetrahedral angle increases with the size of the cation.

The crystal structures try to compensate for the bonding strain, resulting at least from geometric reasons, by varying the atomic coordinates and bond lengths. Position 1 is thereby often partially occupied or occupied by substitution elements, such as transition metals, in particular at their lower concentrations. Defects and substitutional atoms (with the size different from the main host component) at the position 1 lead to a shift of the adjacent atoms at the position 3 and increase the angle deviation from the tetrahedral values which may be even less suitable for the tetrahedral environment (Table 2.1). The reduction of the total energy obtained by substitution seems to compensate the ‘losses’ caused by the stronger deviation from the tetrahedral environment of atoms in the framework.

In the binary type-I clathrates, the formation of vacancies at position 1 allows for the adjustment of the total electronic balance (see chapter 2.3). Crystallographically, the formation of defects at this position, e.g. in $\text{K}_8\text{Sn}_{44}\square_2$ [38] or in $\text{Cs}_8\text{Sn}_{44}\square_2$ [39] goes in parallel with an unusually large atomic displacement anisotropy of position three (Fig. 2.4, middle left). Analysis of the electronic density shows that this anisotropy increases with decreasing temperature (cf. difference electron density maps in Fig. 2.4, middle). For the case of the thermal displacement solely, the anisotropy should be also reduced. Thus two split positions were used for the description of the electron density in this region. Position 31 describes the location of the Sn3 atom when the neighboring Sn1 is present, and position 32 represents the location of the Sn3 atom next to the vacancy $\square$ at the Sn1 position (Fig. 2.4, bottom). Summing up the occupancies of the framework positions leads to the final compositions $\text{K}_8\text{Sn}_{44}\square_2$ or $\text{Cs}_8\text{Sn}_{44}\square_2$.

The formation of defects leads locally to strong changes in the electron density distribution so that four lone pairs are formed around each defect in the framework. Such regions are expected to order within the structure to achieve a more homogeneous distribution of the charge. Indeed, recent detailed studies of the crystal structure of $\text{Ba}_8\text{Ge}_{43}\square_3$ [40, 41], $\text{Rb}_8\text{Sn}_{44}\square_2$ [42] and $\text{Cs}_8\text{Sn}_{44}\square_2$ [43] reveal that the vacancies order within the hexagons along [100] and then within the tetrakaidecahedrons in a way that the distance between the nearest vacancies along the [001] direction is maximized (Fig. 2.5, middle). The symmetry remains cubic

Table 2.1 Distances and bond angles for the framework positions in selected clathrates I

Compound	<i>Distances (Å) and Bond angles (deg)</i>			Reference
	Position 1	Position 2	Position 3	
Na ₈ Si ₄₆	4×2.381	3×2.366	2×2.367	[32]
	4×108.8	1×2.292	1×2.381	
	2×110.9	3×108.9	1×2.396	
		3×110.1	2×105.7	
			1×105.8	
			2×106.9	
Cs _{8-x} Si ₄₆	4×2.440	3×2.398	2×2.398	[37]
	4×107.7	1×2.321	1×2.440	
	2×113.1	3×109.3	1×2.498	
		3×109.7	2×104.8	
			1×106.0	
			2×107.6	
Ba _{8-x} Si ₄₆	4×2.403	3×2.377	2×2.377	[106]
	4×108.0	1×2.329	1×2.403	
	2×112.4	3×109.4	1×2.509	
		3×109.5	2×105.6	
			1×107.6	
			2×106.7	
Ba ₈ Al ₁₀ Si ₃₆	4×2.500	3×2.420	2×2.420	[50]
	4×108.5	1×2.377	1×2.440	
	2×111.4	3×109.2	1×2.500	
		3×109.7	2×104.0	
			1×106.7	
			2×107.4	
K ₈ Sn ₄₆ (refinement without defects at position 1 and split at position 3)	4×2.842	3×2.786	2×2.786	[38]
	4×109.62	1×2.810	1×2.842	
	2×109.18	3×110.45	1×2.717	
		3×108.48	2×105.37	
			1×103.90	
			2×107.45	
K ₈ Sn ₄₄ (refinement with defect at position 1 and split position 3–31 and 32)		2×2.786	2×2.786	[38]
		1×2.810	1×2.842	
		1×3.041	1×2.717 or 1×3.041	
		2×108.48		
		1×97.95	1×103.90	
		1×110.45	2×105.37	
		1×114.13	2×107.45 or 2×112.90	
		1×116.27	1×125.41 or 1×115.37	
			or	
			2×3.041	
			1×3.035	
			1×92.35	
			2×93.80	

Fig. 2.4 Defects in the crystal structure of clathrate-I $\text{K}_8\text{Sn}_{44}\square_2$: (*top*) environment of the Sn1 position in the (100) plane; (*middle*) displacement ellipsoids in the (100) plane without taking into account the splitting of the Sn3 position (*left*) and considering the splitting into Sn31 and Sn32 (*right*) together with the difference density distribution at $T = 300\text{ K}$ and $T = 80\text{ K}$; (*bottom*) different local atomic arrangements without (*left*) and with (*right*) defect at the Sn1 position

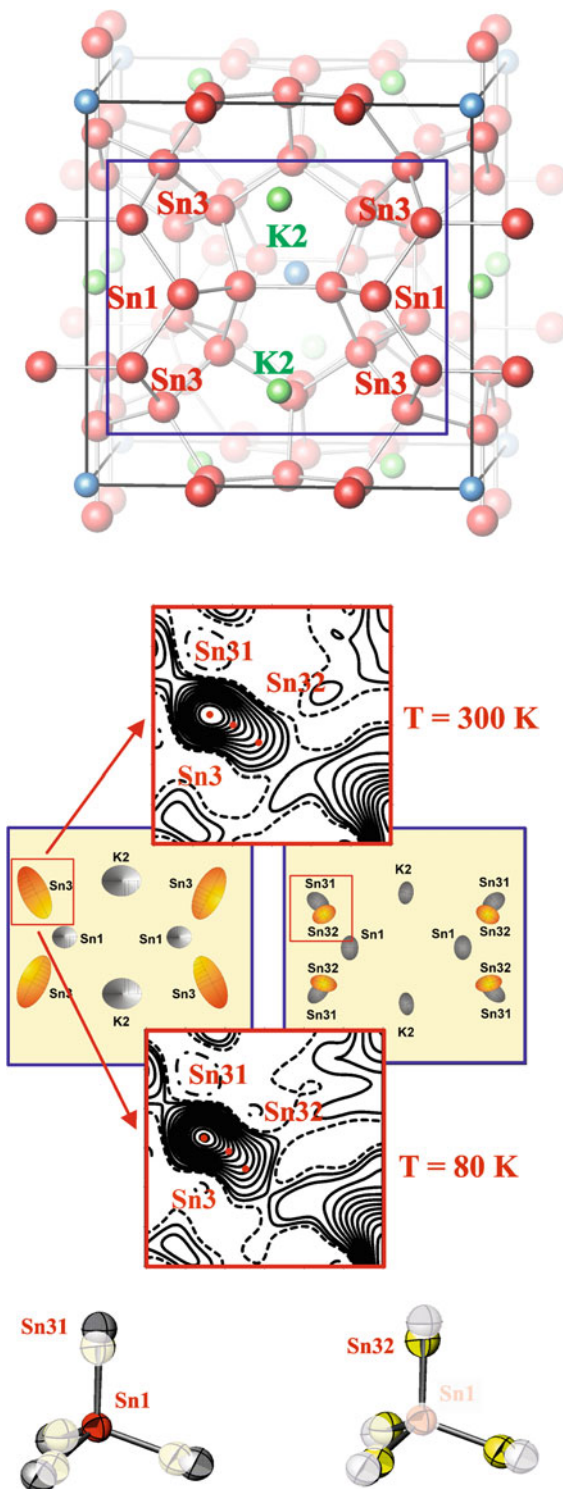
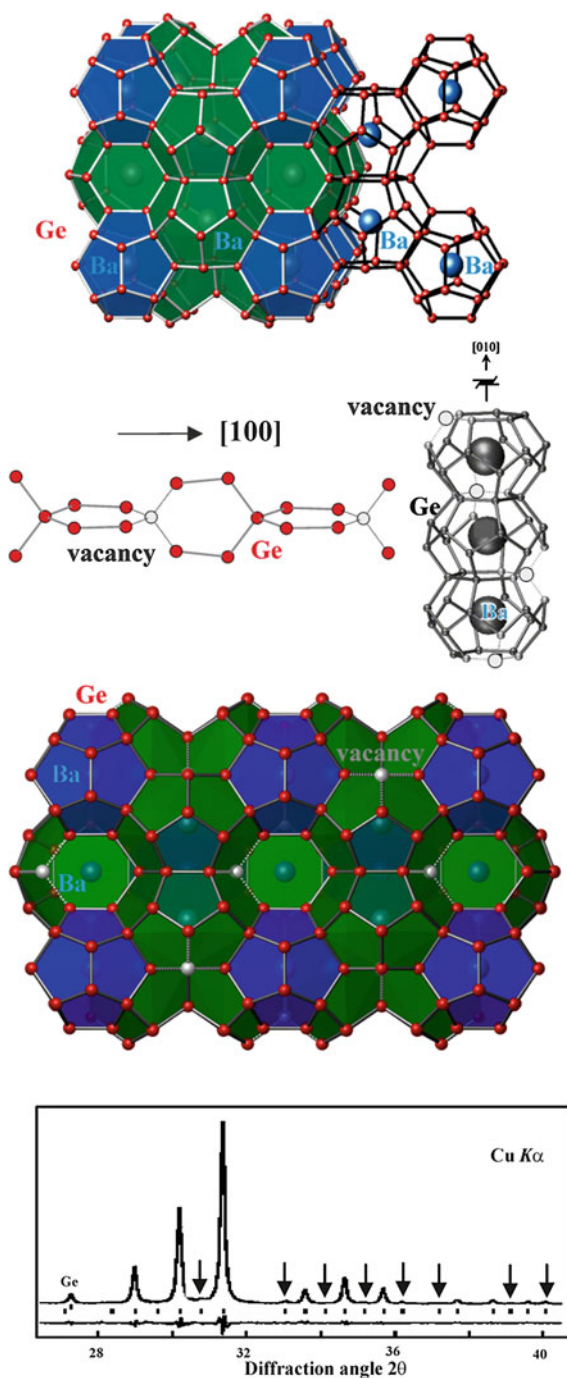


Fig. 2.5 Ordering of defects and formation of the $2 \times 2 \times 2$ superstructure in $\text{Ba}_8\text{Ge}_{43}\square_3$: (*top left*) packing of the polyhedral cages in the clathrate-I type of structure without defects; (*middle left*) ordering of vacancies (grey) within the hexagon chain along [100] direction; (*middle right*) ordering of vacancies within a column of the tetrakaidecahedrons; (*middle*) polyhedron packing in the $2 \times 2 \times 2$ superstructure; tetrakaidecahedrons equal in the original clathrate-I structure, differ in the position of the vacancy; (*bottom left*) occurrence of the superstructure reflections in the X-ray powder diffraction pattern



(space group $Ia\bar{3}d$), the unit cell parameter doubles (cf. powder diffraction pattern in Fig. 2.5, bottom), the volume of the unit cell is eight time larger, and the resulting unit cell contains 432- x atoms (e.g. for $\text{Ba}_8\text{Ge}_{43}\square_3$, $8 \times 54 - 8 \times 3 = 432 - 24$ atoms in the unit cell, Fig. 2.5, middle). For the tin clathrates, superstructure reflections appear in the diffraction patterns provided that the crystallization of the products is realized slow enough or the products were annealed for a long time at an appropriately low temperature [43]. This may explain why superstructure formation was not observed in previous investigations of $\text{Ba}_8\text{Ge}_{43}\square_3$ [44] or $\text{Cs}_8\text{Sn}_{44}\square_2$ [39] or was observed to different extent in different crystals of $\text{Ba}_8\text{Ge}_{43}\square_3$ [40].

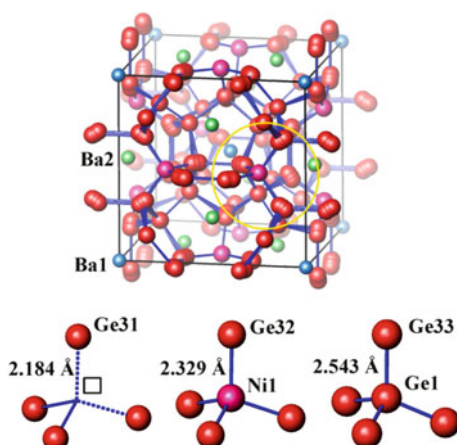
Another way to release the bonding strain in the framework and at the same time adjust the total electronic concentration in a clathrate system is substitution of the p -elements in the framework by other p - or s -elements or transition metals. Studies in the system Ba–Ni–Ge show that for small amount of nickel it formally fills the vacancies of a hypothetical binary Zintl phase ‘ $\text{Ba}_8\text{Ge}_{42}\square_4$ ’ [45]. Only for higher Ni contents the nickel atoms start to replace germanium in the framework [46]. For the composition $\text{Ba}_8\text{Ni}_{3.5}\text{Ge}_{42.1}\square_{0.4}$ the crystal structure around the positions 1 and 3 is complex (Fig. 2.6, top). The distribution of the electron density around position three cannot be satisfactorily described applying one atom with a large anisotropic displacement. In order to describe the electron density in the vicinity of Ge3 correctly, three split positions are required. The first (31) if a vacancy is present at position one (Fig. 2.6, bottom left), the second (32) if position 1 is occupied by Ni (Fig. 2.6, bottom middle), and the third (33) for position 1 being occupied by Ge (Fig. 2.6, bottom right). The distance between the positions 1 and the split positions around 3 vary reliably from ≈ 2.2 Å (to 31) to 2.5 Å (to 33).

A similar complex disorder was observed in the study of the inverse clathrates-I compounds $\text{Sn}_{19.3}\text{Cu}_{4.7}\text{As}_{22}\text{I}_8$ [47], $\text{Sn}_{20}\text{Zn}_4\text{P}_{22-\nu}\text{I}_8$ ($\nu = 1.2$), $\text{Sn}_{17}\text{Zn}_7\text{P}_{22}\text{I}_8$, and $\text{Sn}_{17}\text{Zn}_7\text{P}_{22}\text{Br}_8$ [48]. In the latter, zinc and tin are occupying position 3, whereas phosphorus is located at positions 1 and 2. This leads to a strong crystallographic disorder around the position 3 which requires three split positions for correct description of the electron density in this region.

2.3 Chemical Bonding: From the Zintl Concept to the Electron-Localizability Approach

Considering the binary and ternary representatives of the clathrate structures in metallic systems, one immediately recognizes enormous chemical variability in the realization of the same structural motif. The framework may play the role of the anion ($\text{Na}_8\text{Si}_{46}$) or of the cation ($\text{Ge}_{38}\text{P}_8\text{I}_8$) or be neutral ($\square_{24}\text{Ge}_{136}$). In the first two cases, the cavity atoms provide charge compensation; in the third one, the cavities remain empty. Several variants for replacement of the main-group elements within the framework are found. While a substitution by another p element can be expected from the chemical point of view (e.g. $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ [24, 49] or $\text{Ba}_8\text{Al}_{10}\text{Si}_{36}$ [50]),

Fig. 2.6 Crystallographic disorder in clathrate-I $\text{Ba}_8\text{Ni}_{3.5}\text{Ge}_{42.1}\square_{0.4}$: (*top*) average structure with split positions around Ge3, the yellow circle encloses the (Ni,Ge)1 position (pink) and the split positions around position three; (*bottom*) local atomic arrangements around the position (Ni,Ge)1 in case it is not occupied (*left*), occupied by Ni (*middle*), and occupied by Ge (*right*) with the resulting interatomic distances



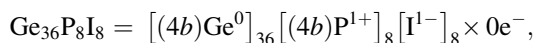
the incorporation of transition elements [51] and—especially—alkali metals ($\text{Cs}_{30}(\text{Na},\text{Sn})_{172-x}$ [36], $\text{K}_8\text{Li}_x\text{Ge}_{46-x}$ [52]) in the framework appears on the first glance surprising and requires additional knowledge about the atomic interactions within the framework. On the other hand, recent studies address additional questions about the role of the species filling the polyhedral cages. A typical understanding of filling atoms as charge donors for the framework assumes their ionic interaction with the framework. The example of the gold-containing clathrate $\text{Ba}_8\text{Au}_{5.3}\text{Ge}_{40.7}$ reveals that the Ba-framework relation is not limited solely to charge transfer and additional Ba–Au interactions have been found [53].

Also the non-monotonic behavior in the lattice parameter of $\text{Na}_{24-x}\text{Si}_{136}$ as a function of the sodium content cannot be explained with ionic interaction alone. One would expect a monotonic increase of the lattice parameter due to the filling of anti-bonding states of silicon. But for $x < 8$ the lattice parameter shrinks, and only for $x > 8$ does it increase with the filling [31, 34]. Furthermore, an ^{7}Na ESR study for low sodium concentrations did not reveal complete charge transfer [54, 55] being in agreement with the NMR investigations [56, 57], and the semiconducting behavior is preserved for $x \leq 4$ [58]. These findings as well as information about the more or less extended homogeneity ranges for many ternary clathrates (caused by substitution in the framework and defects at the guest sites) raise the question about the general picture of atomic interactions in clathrates.

2.3.1 Zintl–Klemm Concept for Clathrates

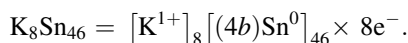
The simplest crystal structure built of four-bonded atoms is that of diamond. Each carbon atom has four shortest distances to its neighbors. Each atom has four valence electrons, which allows interpretation of all the short contacts as two center-two electron ($2c-2e$) bonds. The simplest heteroatomic structure built the same way is the

structure of sphalerite, ZnS. Each zinc atom is surrounded by four sulfur atoms and vice versa. The average number of electrons per atom is also four, thus here all bonds can be considered as $2c-2e$ bonds. The diamond and the sphalerite structures can be interpreted applying the usual valence rules. The condition for the validity of this interpretation is that a sufficient number of electrons is available in the system to realize all the bonds (crystallographically the shortest distances) as $2c-2e$ bonds. In the unit cell of the clathrate-I motif, e.g. in $\text{Na}_8\text{Si}_{46}$, there are 92 short contacts within the framework, comparable with the sum of the covalent radii of the participating atoms ($d(\text{Si-Si}) = 2.292 - 2.381 \text{ \AA}$, $2r_{\text{cov}}(\text{Si}) = 2.34 \text{ \AA}$ [59]). Further 184 shortest contacts between the guest and the framework atoms are larger than the sum of the corresponding atomic radii ($d(\text{Na-Si}) = 3.269 - 3.358 \text{ \AA}$ in the pentagon-dodecahedron and $d(\text{Na-Si}) = 3.432 - 3.944 \text{ \AA}$ in the tetrakaidecahedron, $r_{\text{at}}(\text{Si}) + r_{\text{at}}(\text{Na}) = 1.17 + 1.53 = 2.70 \text{ \AA}$ [59]). The available 192 valence electrons are not sufficient to form $2c-2e$ bonds between Na and the surrounding Si atoms in the Si_{20} and Si_{24} cages. This situation is characteristic of the majority of inter-metallic compounds [60]. In order to apply the Zintl-Klemm concept to clathrates only the bonds within the framework are considered as $2c-2e$ bonds. The average number of valence electrons per framework atom should be four, and each atom obtains a formal charge (which may be used as oxidation number) $n_{\text{val}} - n_{\text{bonds}}$, where n_{val} is the number of valence electrons according to the Periodic Chart and n_{bonds} is the number of bonds in which the atoms participates. The interaction between the guests and the framework is understood as charge transfer: in the anionic clathrates, the guest cations deliver their valence electrons to the framework; in case of the cationic (inverse) clathrates, the guest anions accept the excess electrons from the framework. For the cationic clathrate $\text{Ge}_{36}\text{P}_8\text{I}_8$ we therefore obtain the complete electronic balance:

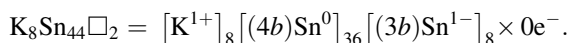


where $4b$ stands for four-bonded atom.

Applying the same recipe to binary germanium and tin clathrates of alkali metals one obtains an unbalanced situation considering a complete host framework:



To accommodate the electrons of the cation, two defects are formed per formula unit in the crystal structure (Fig. 2.4). The eight neighboring tin atoms are three-bonded, thus they obtain the oxidation number of -1 , and the total balance is electron precise:



Application of the Zintl-Klemm concept allows complete understanding of the composition and defects in the crystal structure of the binary germanium and tin

clathrates-I of alkaline metals according to the formula $A_8E_{44}\square_2$ [61, 62]. This concept is also effective in understanding the presence of vacancies in the guest substructure of ternary alkali-metal clathrates with p -elements, e.g.

$$K_7Si_{39}B_7 = [K^{1+}]_{8-1}[(4b)Si^0]_{39}[(4b)B^{1-}]_7 \times 0e^-$$

[63], or for the interpretation of the ideal content of the substituting elements in many ternary clathrates with p elements and even transition elements as substitution components such as

$$Ba_8Ge_{30}Ga_{16} = [Ba^{2+}]_8[(4b)Ge^0]_{30}[(4b)Ga^{1-}]_{16} \times 0e^-$$

[24, 49], or

$$Ba_8Ge_{40.67}Au_{5.33} = [Ba^{2+}]_8[(4b)Ge^0]_{40.67}[(4b)Au^{3-}]_{5.33} \times 0e^-$$

[53].

The complete balance in the sense of oxidation numbers derived in such a way is not a general feature of clathrates. In particular, the defect structure of the alkaline-earth metal clathrate $Ba_8Ge_{43}\square_3$ shows a balance with excess electrons:

$$Ba_8Ge_{43}\square_3 = [Ba^{2+}]_8[(3b)Ge^{1-}]_{12}[(4b)Ge^0]_{31} \times 4e^-.$$

All binary silicon clathrates show even larger numbers of excess electrons, e.g.

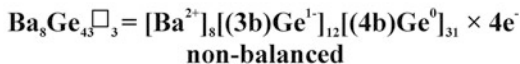
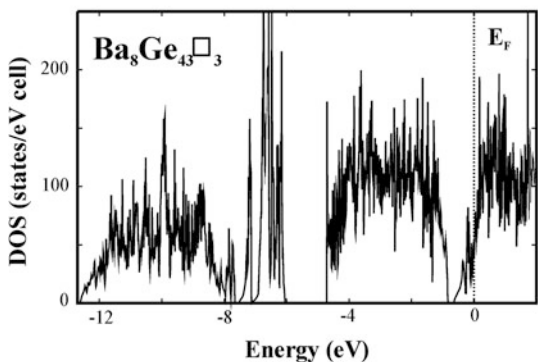
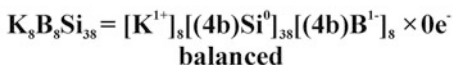
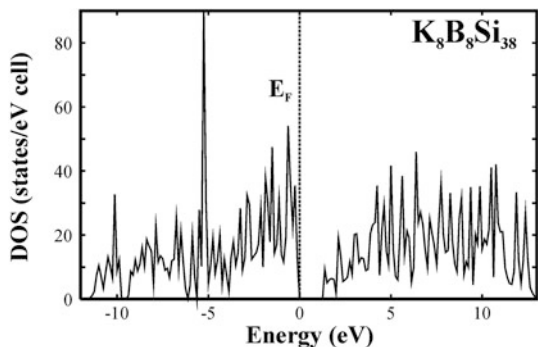
$$Na_8Si_{46} = [Na^{1+}]_8[(4b)Si^0]_{46} \times 8e^-.$$

Besides the possibility to understand chemical composition and structural features, the balances above are connected to the electronic density of states, DOS (Fig. 2.7). In the case of a completely balanced situation, the Fermi level is located in a gap or pseudo gap of the calculated electronic DOS indicating a semi-conducting or bad-metal behavior in electronic transport. If excess electrons are present, the Fermi level is located in the conduction band, suggesting n -type metallic or metal-like electronic transport.

In contrast to the intermetallic anionic clathrates, the cationic clathrates mainly show an electron-balanced situation or very small deviations thereof. Thus the Zintl–Klemm concept provides an adequate tool to describe the general picture of atomic interactions in cationic (inverse) clathrates. In anionic clathrates deviating from the Zintl–Klemm concept mostly excess-electron situations are observed. P -type conduction, which can be considered as a physical ‘fingerprint’ for electron deficiency, is less common. Besides the known results on $Ba_8Ga_{16+x}Ge_{30-x}$ [64], such behavior was found recently for $Ba_8Au_{5.3}Ge_{40.7}$ [53] and $Ba_8Au_xSi_{46-x}$ ($x > 5.43$) [65, 66].

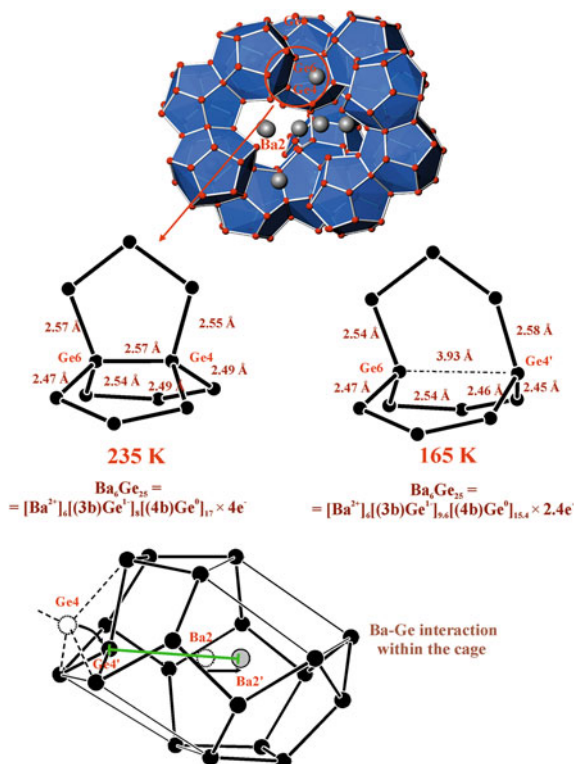
Assuming that the $2c$ - $2e$ covalent-bond description is sufficient for the interpretation of chemical bonding within the framework of anionic clathrates, the

Fig. 2.7 Electron balance and calculated electronic density of state for the clathrates-I $K_7Si_{39}B_7$ (idealized composition $K_8Si_{38}B_8$) and $Ba_8Ge_{43}\square_3$



excess electrons may be thought of as contributing to the guest-framework interactions. A clear experimental hint to the special features of these interactions was obtained for the clathrate *cP124* Ba_6Ge_{25} (Fig. 2.8) [67]. The temperature dependence of the lattice parameter exhibits two anomalies at about 180 and 230 K, caused by a structure transformation in two steps. A reconstructive nature of the structural transformation involves Ge–Ge bond breaking and barium cation displacement (Fig. 2.8, middle). Some Ge4 type atoms are so significantly displaced during cooling that Ge4–Ge6 bonds break and new three-bonded (3b) Ge^{1-} species (electron acceptors) are formed. Consequently the number of charge carriers is reduced thus affecting the physical properties [68]. The driving force for this transformation is an additional Ba–Ge interaction (Fig. 2.8, bottom) which is obviously more favorable than the Ge–Ge bonding at low temperatures.

Fig. 2.8 Structural phase transformation in clathrate *cP124* $\text{Ba}_8\text{Ge}_{25}$: (*top*) crystal structure with the atomic arrangement relevant for the structural transformation; (*middle*) atomic arrangements and interatomic distances in the vicinity of the Ge4–Ge6 bond above (*left*) and below (*right*) the transformation temperature; (*bottom*) changes in the coordination sphere of the Ba2 atoms caused by the transformation [67]



2.3.2 Electron-Localizability Approach

The discussed guest-framework interactions cannot be studied within the Zintl–Klemm concept, because per definition it restricts them to the Coulomb forces caused by charge transfer. More insight may be achieved by applying quantum chemical tools for the analysis of chemical bonding in real space. The electron localizability approach based on a combined consideration of electron density and electron localizability indicator developed recently provides an efficient technique for the analysis of chemical bonding in intermetallic compounds [69]. The analysis of the topology of the electron density by means of the quantum theory of atoms in molecules (QTAIM [70]) yields the 3D representations of atoms (atomic basins) in real space. The obtained electron density basins represent the individual atoms in the system when a nucleus is contained within the basin. The difference between the electron population of the basin surrounding the nucleus and the nuclear charge yields the charge of the atomic basin, which is often relatively close to the formal charge of the examined atomic species.

The shapes of QTAIM atoms in barium–germanium clathrates at the ideal composition $\text{Ba}_8\text{Ge}_{40}\text{E}_6$ are shown in Fig. 2.9 (top) [71]. Ba atoms show shapes close to spherical. This is in agreement with their role as cations. In such cases the

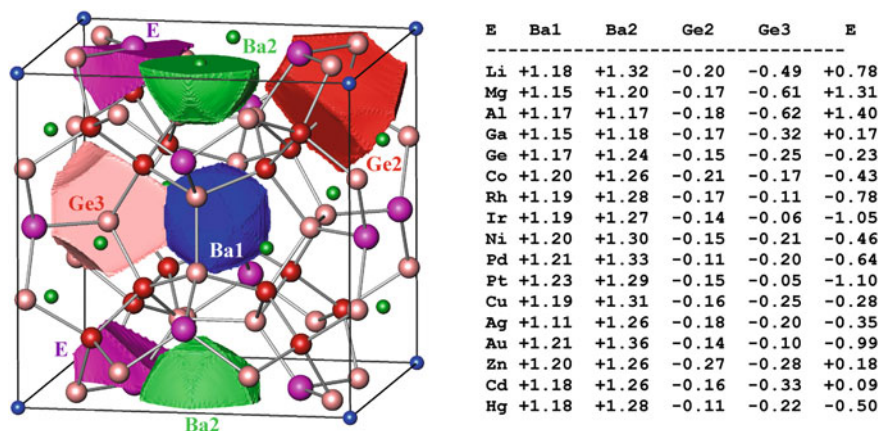


Fig. 2.9 Atomic basins (QTAIM atoms) in the barium–germanium clathrates with the hypothetical composition $\text{Ba}_8\text{Ge}_{40}\text{E}_6$ (left) and the effective QTAIM charges (right)

QTAIM atom should envelop only the inner shells which, in turn, should show a spherical distribution of electron density. The effective charge of both Ba positions is essentially independent of the substitution elements and is much lower than the expected $2+$. The shapes for the Ge2 and Ge3 positions as well as for the E1 position reflect their environment and are far from spherical. This implies that the interaction within the framework and between the guest and the framework is different. The effective charge of the E1 position is strongly dependent on the electronegativity difference between the substitution element E and germanium; the more electronegative E is the more negative charge it accommodates (Fig. 2.9, bottom). The polar character of the Ge3–E1 interaction is also reflected in the charge at Ge3: the more electronegative E is the more positive charge is accommodated at Ge3. The charge of Ge2 coordinated by Ge2 and Ge3 is practically independent of the kind of the substitution element E [71].

Further information about the chemical bonding can be obtained using the electron localizability indicator [72, 73] in its ELI-D representation as a bonding descriptor [74]. ELI-D describes the correlation of electronic motion. It is proportional to the electron population needed to form a fixed fraction of an electron pair. In analogy to QTAIM, ELI-D basins can be determined and assigned to chemically meaningful descriptors. Because ELI-D reveals regions of space that can be used as descriptors of atomic shells, bonds and lone-pairs, the examination of ELI-D may shed more light on the electronic structure of the intermetallic clathrates.

The distribution of ELI-D in the ordered superstructure $\text{Ba}_8\text{Ge}_{43}\square_3$ (Fig. 2.10, top) clearly reveals the covalent interaction between the germanium atoms within the framework [71]. Both three- and four-bonded germanium atoms form direct bonds which are visualized by ELI-D maxima (attractors) located on the shortest Ge–Ge contacts or very close to them (Fig. 2.10, middle right and bottom).

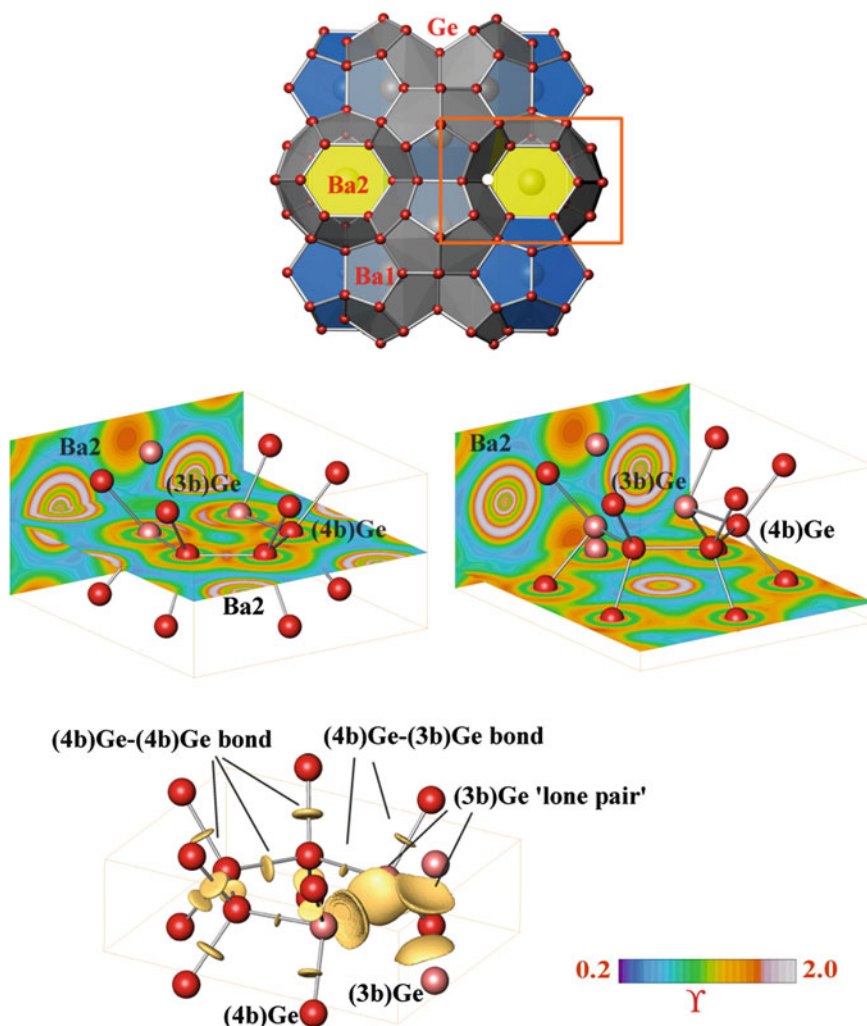


Fig. 2.10 Electron localizability indicator in $\text{Ba}_8\text{Ge}_{43}$: (top) the investigated fragment of the crystal structure; (middle) distribution of ELI-D in the planes of Ba atoms (left) and in the plane of the defect hexagonal face of the tetrakaidecahedron (right); (bottom) isosurface of $Y = 1.25$ visualizing the Ge-Ge bonds and lone pairs at the three-bonded germanium atoms

Furthermore, the lone pairs at (3b)Ge atoms are visualized by the four ELI attractors oriented toward the vacancy position (Fig. 2.10, bottom). The distribution of ELI-D in the inner shells of the Ge atoms is spherical, indicating that, as expected, the electrons of the inner shells do not participate in valence interactions. The striking feature of the ELI-D distribution around the Ba atoms is the missing sixth shell. This suggests charge transfer to the framework and is in agreement with the idea of ionic guest-framework interaction (Fig. 2.10, middle left). The

penultimate shell of Ba is slightly structured—the ELI-D distribution shows a small deviation from sphericity. This finding is a ‘fingerprint’ for the participation of the penultimate-shell electrons in the valence-region interactions [74, 75] revealing a first trend to some additional interactions between Ba and framework aside the ionic one.

Substitution of elements *E* with different electronegativities at the position Ge1, keeping in mind the traditional picture of chemical bonding for $\text{Ba}_8\text{Ge}_{40}\text{E}_6$, causes several changes in the details of the atomic interactions which can be resolved by application of the electron-localizability approach (Fig. 2.11). The last sixth shell of the Ba atoms is not present in all four compounds, supporting basically ionic interaction of Ba with the framework. The Ge–Ge interaction remains covalent being independent of the kind of the element *E*. The combined analysis of the electron density and ELI-D using the intersection technique [76] shows that the Li–Ge (0.04 electrons from Li and 2.3 from Ge) and Au–Ge (1.4 electron from Au and 0.4 from Ge) interactions are polar. With Li, germanium plays therefore the role of electron acceptor, and with Au germanium donates electrons. These findings are also supported by the effective QTAIM charges (cf. above). The inner shell of Au is already structured showing regions with slightly lower values on the Ba–Au contact line, signaling an additional interaction. The same feature is observed for the inner shell of the Ba atoms. The direct Ba–Au interaction is manifested by a separate maximum of ELI-D (Fig. 2.11, bottom right). This kind of interaction is a novel feature for intermetallic compounds and was found for the first time in form of a dedicated maximum in ELI-D distribution for the gold-containing clathrates. Current studies reveal similar features for Pt, Pd and Cd compounds [71].

The application of the electron localizability approach allows for studying details of the atomic interactions in intermetallic clathrates. This may contribute to the understanding of structural features which cannot be achieved within the Zintl–Klemm concept. Another, from chemical point important, outcome of the electron localizability approach is the electron-localizability-based oxidation number (ELIBON [77]) which is the real-space equivalent of the traditional oxidation numbers. Application of oxidation numbers on intermetallic clathrates allows for new ways of understanding of experimentally observed clathrate compositions and for novel redox routes for their preparation.

2.4 Preparation Routes: From Direct Reaction Between Elements to Redox Processes

Various synthesis routes to intermetallic clathrates have been successfully applied covering the whole spectrum of preparation methods in solid state chemistry. The applicability of each method is dependent on the elements forming the target material and some thermodynamic properties, such as formation energy and vapor pressure of components at the reaction temperature. Although it is straightforward for many systems to prepare a clathrate phase at one certain composition,

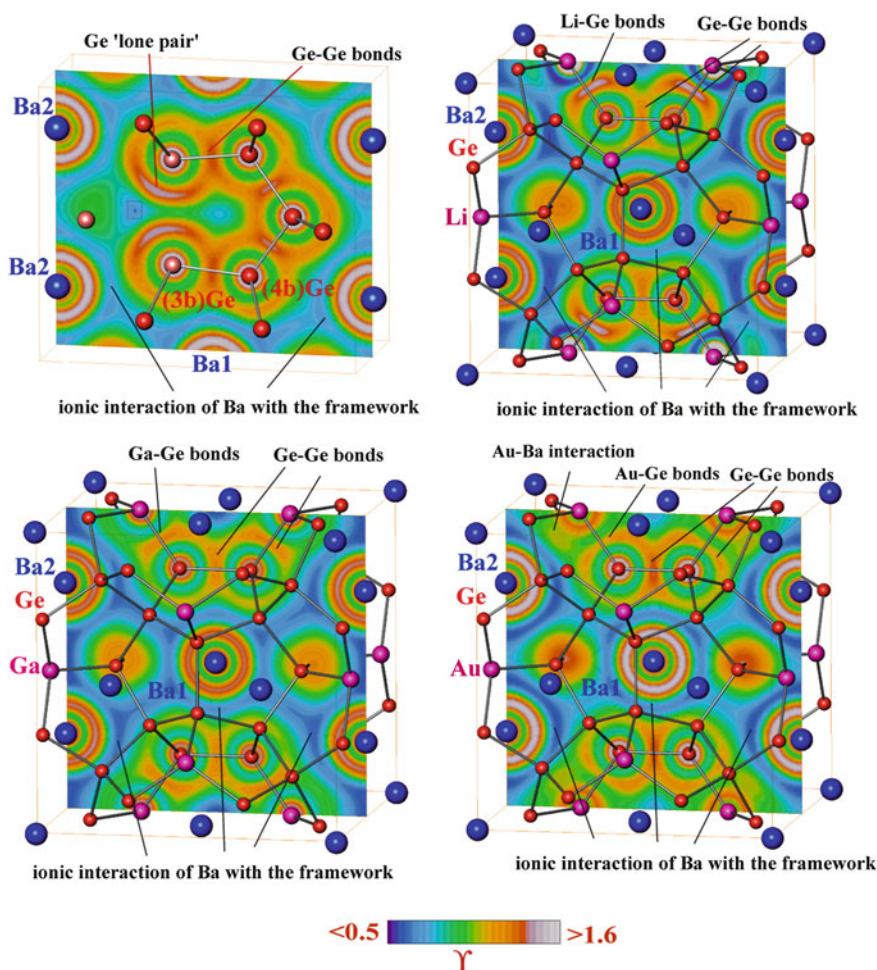


Fig. 2.11 ELI-D distributions in the barium–germanium clathrates $\text{Ba}_8\text{Ge}_{43}\square_3$ (top left, $\square$ stands for vacancy), $\text{Ba}_8\text{Li}_6\text{Ge}_{40}$ (top right), $\text{Ba}_8\text{Ga}_6\text{Ge}_{40}$ (bottom left) and $\text{Ba}_8\text{Au}_6\text{Ge}_{40}$ (bottom right) illustrating the polar and non-polar covalent bonds in the framework, the ionic interaction of Ba with the framework and the additional covalent Ba–Au interaction

systematic investigations of electronic transport behavior require more effort. The correlation of chemical composition and structural defects with intrinsic electronic transport properties resembles the well-known challenges of semiconductor science. However, despite the fact that clathrate research in the literature has been developed into materials science and appears to be mainly focused on energy-related applications, i.e. thermoelectricity, it still holds surprising results and interesting open questions for fundamental investigations. This is also reflected by the ongoing developments of preparation methods which have resulted in new types of clathrate phases after decades of research.

2.4.1 Crystallization from the Melt

In favorable cases, clathrate phases show a high stability and form congruently from the melt. With respect to the clathrate-I type of crystal structure, some ternary materials are prepared with compositions tending to an electronic balance such as $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ [24, 49] and $\text{Ba}_8\text{Au}_{5.33}\text{Ge}_{40.67}$ [53]. Some clathrate-II type phases with homoatomic framework, such as $\text{Na}_{16}M_8Y_{136}$ ($M = \text{Rb}, \text{Cs}$; $Y = \text{Si}, \text{Ge}$), may form congruently as well [78]. The respective melting behavior can be explained by considering the stability of neighboring phases. In this case mixtures, e.g. $M_{12}\text{Si}_{17} + \text{Si}$ or $M_4\text{Ge}_9 + \text{Ge}$, are less stable than, e.g., BaSi_2 and Si . A hindrance for crystal growth can be a large homogeneity range of clathrate phases. If the preparation starts at a composition deviating from the congruently melting one or formation reaction is peritectic, the crystals of the phase having a homogeneity range may show a marked gradient in composition along the growth direction for usual growth rates. A successful method to obtain large single crystals is the *Czochralski* technique. However, due to its technical complexity the application of this method has been restricted to systems with negligible vapor pressures such as $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ [79] and $\text{Ba}_8\text{Al}_x\text{Si}_{46-x}$ [80]. For comparison, equipment and experimental procedures are much simpler for the *Bridgman* technique which allows for the use of welded crucibles. For carbon or metal crucibles with high thermal conductivity the temperature profile in the crystal growth experiment is blurred so that not all experiments are successful and several crystalline grains, instead of a single one, are typically formed. In contrast to glass ampoules, the necking of the ampoule favorable for grain selection is generally not applicable for glassy carbon and metal tubes. Instead, a simple inset with conic wholes can be placed at the bottom of the growth crucible. By using the *Bridgman* technique, mm-sized single crystals of $\text{Ba}_8\text{Ni}_{3.5}\text{Ge}_{42.1}$ [46] and even cm-sized single crystal of $\text{Ba}_8\text{Au}_{5.3}\text{Ge}_{40.7}$ [53] (Fig. 2.12) have been grown in glassy carbon crucibles.

2.4.2 Polycrystalline Samples by Melt Quenching

Some clathrate phases exist in the phase diagram only within a small temperature window. For example, the clathrate $\text{Ba}_8\text{Ge}_{43}\square_3$ is thermodynamically stable at ambient pressure between 770 and 810 °C [41]. By applying slow cooling rates the clathrate phase is decomposed below the stability limit, provided the temperature is still high enough to trigger a solid state reaction. Hence, rapid cooling (quenching) techniques are required for successful preparation. One possibility for quenching is the melt spinning method which is often used to influence the microstructure of clathrate phases, e.g. for $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ [81]. More simple is the steel quenching technique imitating traditional forging. A portion of the melt at the clathrate composition is heated in a glassy carbon crucible, then purged on a cold steel plate and hammered by a second plate (Fig. 2.13). The cooling rate

Fig. 2.12 Microstructure of single crystals of $\text{Ba}_8\text{Ni}_{3.7}\text{Ge}_{42.1}$ (*left*) and $\text{Ba}_8\text{Au}_{5.44}\text{Ge}_{40.67}$ (*right*)

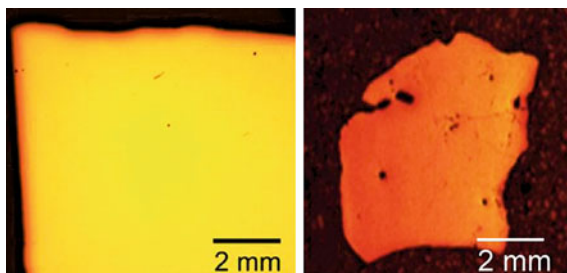
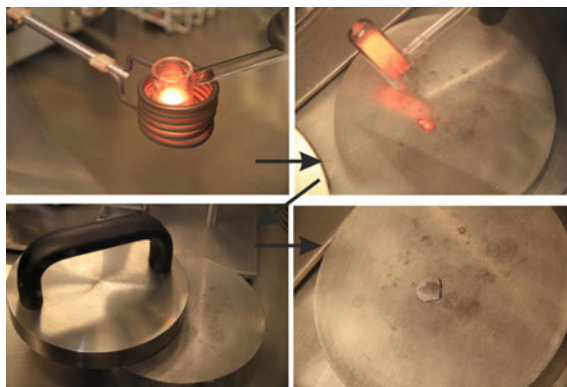


Fig. 2.13 Steel-quenching preparation of polycrystalline clathrate phase



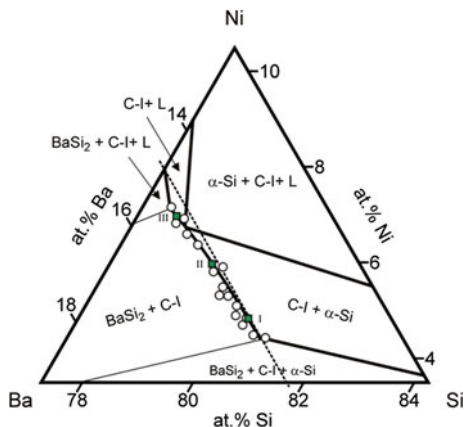
using this procedure is estimated to be higher than 1,000 K/s. In this way single-phase polycrystalline products have been obtained (e.g. $\text{Ba}_8\text{Ge}_{43}\square_3$ [41], $\text{Ba}_8\text{Ir}_{0.2}\text{Ge}_{43}\square_3$ [82]), and superconducting $\text{Ba}_8\text{Ni}_1\text{Si}_{45}$ has been stabilized in the metastable ambient pressure region [83].

For melts with high vapor pressure, both methods described above cannot be applied and closed ampoules must be used instead. In this case it has turned out to be useful to purge water directly on the heated metal container instead of throwing metal tubes with quartz jacket into water, as typically described in the literature. Due to the vigorous steam development of water at 1,000 °C this method requires special equipment and safety arrangements. When moderate cooling rates are sufficient, arc melting may be applied as well [84]. The method is, however, suitable only, when no marked evaporation losses appear during arc melting since these can be only roughly corrected by weighing excess amounts of the volatile components.

2.4.3 Solid State Reactions

To investigate homogeneity ranges and the relationship between physical properties and chemical composition, the equilibrium state for each composition has to be achieved. The ampoules or crucibles along with the starting materials are placed in vertical tube furnaces with well-controlled temperature profile (control

Fig. 2.14 Phase relations for $\text{Ba}_8\text{Ni}_x\text{Si}_{46-x-y}$ at 1,000 °C. Analysis of the equilibrium phases after annealing clearly shows the deviation of the homogeneity range from the iso-concentration line describing the composition $\text{Ba}_8\text{Ni}_x\text{Si}_{46-x}$ and hence the presence of defects in the silicon framework [83]



measurements should be done before each annealing experiment). The annealing times depend strongly on the system studied. For example the clathrate $\text{Ba}_8\text{Ni}_x\text{Si}_{46-x-y}$ [83] is typically obtained as a single-phase material after annealing for one week at 1,000 °C (for phase equilibria, see Fig. 2.14), and the germanium clathrate $\text{Ba}_8\text{Ni}_x\text{Ge}_{46-x-y}$ —after 1 week at 800 °C. The crucible material for silicon clathrates is typically corundum, for those of germanium (without alkali metals)—glassy carbon, for tin compounds—glassy carbon or metal, and for phosphorus representatives—quartz glass. An appropriate crucible material can only be identified taking into account its interaction with all components used for the synthesis. Side reactions with the container material can often be easily realized but can also lead to misconceptions. For example when a clathrate at composition $\text{Ba}_8\text{Ni}_4\text{Ge}_{42}$ is annealed in Ta ampoules, the neighboring clathrate phase $\text{Ba}_6\text{Ge}_{25}$ appears in the reaction product, which is widely inert against Ta, while TaGe_2 is formed at the container wall [85].

If the clathrate develops a significant vapor pressure on heating, the reaction crucible must be welded in a metal tube. For the outer metal tube the choice of material is less critical, and stainless steel is just as good as expensive tantalum. The annealing process can be shortened by careful homogenization of the starting mixture, but there are systems like clathrate phosphides for which even long-time annealing is not sufficient. Here a clathrate phase can be only obtained by several annealing steps with repeated milling and compacting [86]. More recently, our studies show that the spark plasma sintering (SPS) allows for distinctly shorter annealing time. However, the respective phase must be stable against electrochemical decomposition during SPS treatment.

2.4.4 Thermal Decomposition

Thermal decomposition of alkali metal monosilicides $M_4\text{Si}_4$ and monogermanides $M_4\text{Ge}_4$ was historically the first preparation method for the respective clathrate

phases in 1961 [87, 88] and it was used in 1995, when the superconducting phase $\text{Na}_2\text{Ba}_6\text{Si}_{46}$ was found. This was the first clathrate phase containing Ba atoms in a complete homoatomic silicon framework [89]. The decomposition experiments are typically performed in the temperature range 300–500 °C in which most crucible materials can be used. The method is best suitable for clathrate products which are not decomposing at the reaction conditions. A more serious problem, however, is the reproducibility of the experimental conditions. In the literature, dynamic vacuum conditions are generally used, but the actual pressure of the volatile particles at the sample position in the reactor is typically not well controlled. As a rough approximation, the counter pressure of the volatile component depends on the temperature of its precipitate forming at the colder part of the reactor. For a long time thermal decomposition experiments yielded only microcrystalline powders, and the investigation of the so-obtained very small single crystals by XRD was challenging [90]. Further development of the decomposition preparation route came up recently with the decomposition experiments of monosilicides in a closed system using a graphite acceptor in shifting the equilibrium [91–94]. The alkali metals are absorbed by the graphite providing a distinct counter pressure of the alkali-metal vapor. This way, mm-sized single crystals of silicon clathrates were obtained.

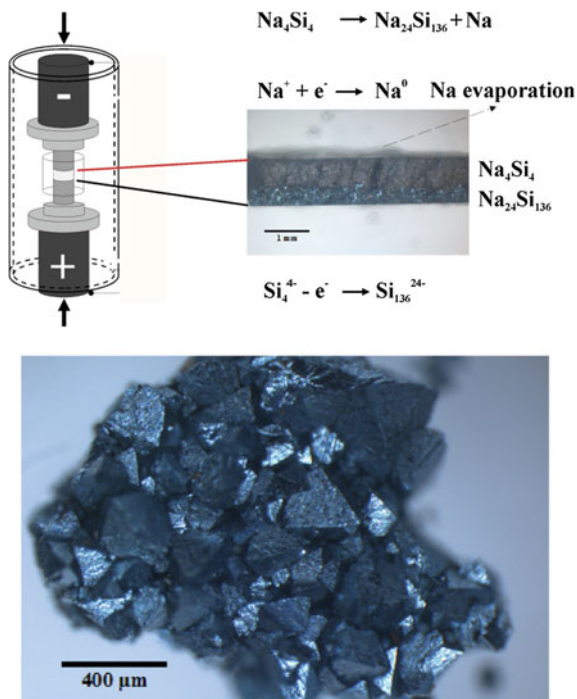
2.4.5 Chemical Transport

The historically first experiment of this kind for clathrates was an attempt to synthesize a noble gas clathrate $\text{Xe}_8\text{Ge}_{46}$ by chemical transport of Ge with GeI_4 under high Xe gas pressure. While the existence of the noble gas clathrates is still under discussion, the first “inverse” clathrate $\text{I}_8\text{Ge}_{43.33}\text{I}_{2.67}$ [95] was obtained in this way. The technique was also successfully applied for the preparation of phases such as $\text{Ge}_{38}\text{As}_8\text{I}_8$ [18]. Later it was developed into a fruitful synthetic tool with the possibility to obtain well-developed single crystals [19, 20].

2.4.6 High-Pressure Synthesis

The anticipation of clathrates as high-pressure phases was not natural due to their bulky host framework. In particular it is not expected that large filler atoms such as Ba and Cs form high-pressure phases. Therefore the first high-temperature high-pressure preparation of the binary silicon clathrate $\text{Ba}_{8-x}\text{Si}_{46}$ by reacting BaSi_2 and Si under high pressure conditions was a sensational report [96]. Later, $\text{Ba}_6\text{Si}_{25}$ [97], $\text{Cs}_{8-x}\text{Si}_{46}$ [37] and $\text{Cs}_{8-x}\text{Ge}_{46-y}$ [98] were prepared at extreme conditions. In fact, clathrates with oversized filler atoms are not stabilized by high pressure, but the competing phases are more destabilized. Generally, high-pressure reactions allow for the preparation of single crystals but can only be performed with small reaction volumes.

Fig. 2.15 Spark-plasma electrochemical redox preparation of clathrate $\text{Na}_{24}\text{Si}_{136}$ (top) and the so-obtained single crystals (bottom) [35]



2.4.7 Electrochemical Clathrate Preparation by the Spark-Plasma Technique

Spark-plasma sintering has been known as an efficient compaction method. This also makes it of special importance for clathrate products. Microcrystalline powders can be transformed under inert atmosphere in special pressure tool to polycrystalline specimens of high density allowing for the determination of physical properties. However material problems must also be solved with the limitation that a part of the tool (die and/or punches) should be manufactured from a conductive material. Recently, new synthetic features of SPS processing were revealed with the preparation of mm-sized single crystals of $\text{Na}_{24}\text{Si}_{136}$ [35] (Fig. 2.15). The synthesis was achieved by electrochemical transformation of Na_4Si_4 at the punches of the SPS tool. Since the first report [17], the preparation of a completely filled clathrate II $\text{Na}_{24}\text{Si}_{136}$ was difficult, and only microcrystalline powders were reported. Hence, this new method opens a route for investigation of the intrinsic physical properties of high-quality large single crystals [99, 100].

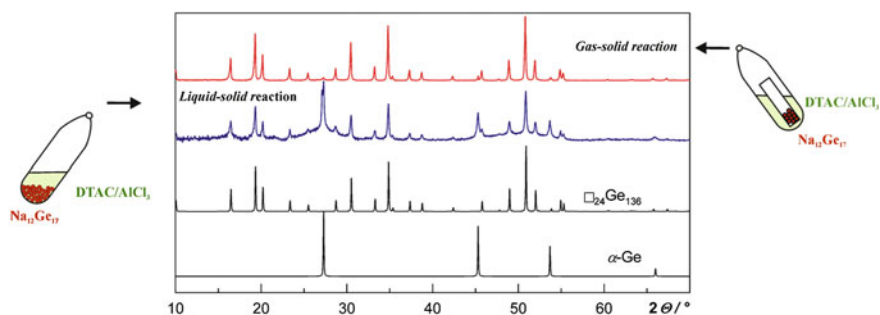


Fig. 2.16 Schematic reaction set-ups for the oxidation of Zintl phases to clathrates (*left* and *right*) and the X-ray powder diffraction patterns of the products of the reactions (*middle*)

2.4.8 Clathrates by Redox Preparation

The established preparation methods described so far need appropriate temperature conditions to achieve full conversion of the reaction educts to the clathrate phase. Alternatively, suitable precursors such as K_4Si_4 or K_4Ge_4 can be converted at relatively low reaction temperatures to clathrate phases by heterogeneous liquid–solid redox process. Due to the low reaction temperatures, metastable phases have been stabilized as well. These products are not accessible at any (p, T) -condition in thermal equilibrium. The method became known when the Zintl phase $\text{Na}_{12}\text{Ge}_{17}$ was reacted in the ionic liquid $\text{DTAC}/\text{AlCl}_3$ to a new allotrope of germanium with empty clathrate-II structure, $\text{Ge}(cF136)$ [101]. Further research on the new products was hindered self-decomposition of the ionic liquid, leading to irreversible contamination of the products. The preparation concept was then further transformed to a gas–solid reaction [102, 103]. In a simplest procedure, suitable educts like Na_4Si_4 and NH_4Cl are placed separately in open glass tubes. These are sealed in a bigger glass ampoule which is heated to the reaction temperature (Fig. 2.16). The reaction product consists of clathrate-I phase and NaCl which can be easily washed out [102]. Alternatively the precursors can be placed under mild conditions in a gas stream of oxidizing agent, e.g. organic chloride. This approach has provided in a short time interesting metastable intermetallic phases and promises new perspectives in the preparation not only of clathrate phases. This is testified by the preparation of elemental allotropes [101] or preparation of high-pressure phase $\text{Ba}_{8-x}\text{Si}_{46}$ at ambient pressure [104], and selective phase preparation [105].

2.5 Outlook: From Flamboyant Substances to Materials of Interest

Within 50 years since their discovery intermetallic clathrates have developed from flamboyant substances with esthetic crystal structures to a materials family with widely investigated properties. Despite remarkable progress in their study, the description and understanding of the crystal structures and chemical bonding in clathrates, a detailed and—at the same time general—picture of the atomic interactions is missing. For example, a prediction of the chemical composition for the homogeneity ranges is currently out of reach. While the composition and the structural features of the frameworks are usually well represented by (polar) covalent bonding between the host atoms, quantitative interpretation of the guest–host interactions remains an open and is key issue for further studies.

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The Physics and Chemistry of Inorganic Clathrates

Nolas, G.S. (Ed.)

2014, XIV, 332 p. 140 illus., 42 illus. in color., Hardcover

ISBN: 978-94-017-9126-7