

Inorganic clathrate-II materials of group 14: synthetic routes and physical properties

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Crystalline open-framework and nanoporous materials have long attracted the attention of chemists, physicists, and materials scientists. The intriguing structures such materials exhibit are often intimately related to the unique physical properties they possess. This article reviews recent developments in the preparation and characterization of one such class of inorganic materials, those comprised of group 14 elements crystallizing with the clathrate-II crystal structure. These materials correspond to expanded forms and, in some cases, metastable allotropes of Si, Ge, and Sn. Just as interesting as the structure and properties that group 14 clathrate-II materials display is the diverse range of synthetic techniques used to prepare them and these techniques are discussed. We review the work to date characterizing the physical properties of group 14 clathrate-II materials with emphasis placed on structure–property relationships, in particular with regard to the electronic and transport properties.

Introduction

The chemistry and physics of group 14 elements such as silicon and germanium have been extensively studied, largely due to their fundamental importance in the development of semiconductor electronics. In addition to their ground state configurations (e.g. the diamond structure for silicon and germanium), these elements can crystallize in metastable expanded framework allotropes,^{1,2} as well as highly stable binary,^{3–6} ternary,^{7–9} and higher order compounds,^{10,11} known collectively as clathrates.†

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† The terms clathrate, inorganic clathrate, and clathrate-II materials strictly speaking can refer to a wide range of materials (clathrate hydrates, clathrasils or metal cyanides, for example). For simplicity and convenience within this article, unless otherwise indicated, these terms shall be used interchangeably to refer to those clathrates derived from elements of group 14, as is common practice in the literature.

Prior to the discovery of inorganic clathrates based upon elements of group 14, analogous structures had been known in gas and liquid hydrates, which constitute expanded forms of ice.^{12–14} Typically stable only at relatively high pressures and low temperatures, these crystalline hydrate phases are formed by a hydrogen bonded framework of water, which can encapsulate a range of organic molecules, noble gases, and even molecular hydrogen.¹³

The existence and structure of group 14 clathrates was first reported by Kasper *et al.*,³ with systematic investigations undertaken by Cros *et al.* soon thereafter.^{15–18} The common structural feature of all clathrate materials is an open-structured host framework that has the ability to encage guest atoms or molecules. The relationship between the structure of these materials and the properties they display is of scientific and technological importance.

In the past ten years there has been a surge in interest in inorganic clathrates derived from the group 14 elements. The drive behind the increased attention given to these materials is



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predominantly two-fold. One, is the wide variety of unusual and intriguing physical properties they display, such as glasslike thermal conductivity,¹⁹ superconductivity in sp^3 bonded solids,^{20,21} magnetism,^{22–25} and heavy atom tunneling in the crystalline state.^{26–28} Two, is the promise they hold for useful applications, ranging from thermoelectrics,^{29–32} to photovoltaics and optoelectronics,^{33–36} to potentially ultra-hard materials.³⁷

There are several structural types that comprise the family of clathrate phases.³⁸ Of these, the group 14 clathrate-I materials have been studied extensively, and several reviews exist for the interested reader.^{38–43} Herein, we review the synthesis and characterization of an emerging class of open-structured materials, those derived from group 14 elements crystallizing with the clathrate-II structure. We focus primarily on the experimental results, though we also discuss theoretical work where pertinent. A rich collection of theoretical treatments may be found in the literature.^{33–36,44–63}

Structure, bonding, and crystal chemistry

As with other group 14 clathrates, the clathrate-II crystal structure can be visualized in terms of face-sharing polyhedral cages resembling fullerene-like building blocks of silicon, germanium, or tin. However, an important difference between the clathrate-II structure and other fullerene solids (*e.g.* crystallized C_{60})⁶⁴ is the tetrahedrally coordinated sp^3 -like bonding found in the clathrates. This can be viewed as a direct consequence of the preference of silicon and germanium (and sometimes tin) for forming sp^3 bonds, whereas carbon readily forms both sp^3 - and sp^2 -like bonds.^{65,66} Whether carbon can crystallize with the clathrate-II structure remains an open experimental question.⁵⁴

The clathrate-II framework is formed by eight 28-membered hexakaidecahedra (E_{28} , point symmetry T_d), and sixteen 20-membered pentagonal dodecahedra (E_{20} , point symmetry I_h) per conventional unit cell, as shown in Fig. 1. The guest atoms reside inside these polyhedra formed by the framework. There are three crystallographic sites (space group $Fd\bar{3}m$) in the framework, 96g, 32e, and 8a in the Wyckoff notation. The guest species reside at the 8b and 16c sites, inside the E_{28} and E_{20} cages, respectively. The resulting structure is face-centered cubic (see Fig. 1), and the general chemical formula can be written as $A_8B_{16}E_{136}$ (A = guest in E_{28} , B = guest in E_{20} , and E = Si,

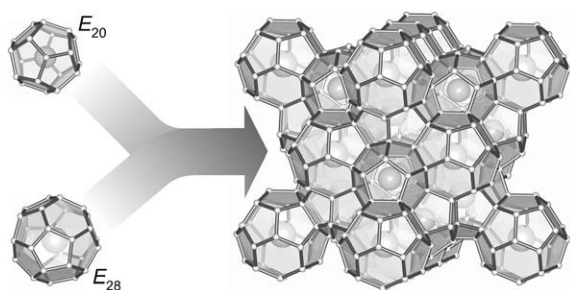


Fig. 1 Sixteen pentagonal dodecahedra (E_{20}) and eight hexakaidecahedra (E_{28}) share faces to form the clathrate-II crystal structure. The smaller light-colored atoms represent the covalently bonded framework, whereas the larger dark-colored atoms represent the guests. The polyhedral cages in the clathrate-II structure may be either completely filled or completely empty, or varied between the two extremes.

Ge, Sn or substituents) in the conventional unit cell. Although qualitative similarities exist between the clathrate-II structure and other group 14 clathrate types, at least one important difference should be emphasized. This is the ability to fully vary the guest concentration in the clathrate-II materials,⁴ whereas the guest content is empirically fixed at full occupation in, for example, the group 14 derived clathrate-I compounds, with very few exceptions. As discussed below, this feature has significant implications for the physical properties of these materials.

As evident from Fig. 1, the clathrate-II framework is composed of 5-membered and 6-membered rings, corresponding to the faces of the E_{20} and E_{28} polyhedra. This is in contrast to the diamond structured phases of the Group 14 elements, which exhibit exclusively 6-membered rings. Indeed, the average number of atoms per ring in the clathrate-II structure is 5.064, and is the smallest of any such known structure.^{33,47} Some of the interesting properties of these materials have been attributed to this large concentration of 5-membered rings.⁶⁷

Some structural analogies exist between the clathrate-II structure and other known compounds and structures. For example, the guest atom positions (8b sites) inside the larger E_{28} polyhedra form an enlarged “diamond lattice”. The E_{28} polyhedra are centered on these sites, with the E_{20} polyhedra being formed in the space between the E_{28} cages. The clathrate-II structure may also be considered as dual to the $MgCu_2$ structure, in the sense that the constituent guest atom positions in the clathrate-II structure (centers of the E_{20} and E_{28} polyhedra) correspond to the positions of the atoms in the $MgCu_2$ structure (*i.e.*, $E_{20} \rightarrow Cu$, $E_{28} \rightarrow Mg$). The interested reader is referred to the literature for more detailed discussions of the various interesting structural and geometric relationships found in clathrate materials.^{38,47,68–70}

In Fig. 2 a plot of the ratio of the free cavity diameter (D) to cage-atom diameter (d) for several cage-like materials is shown as a function of the square root of the number of atoms in the cage, *i.e.* the coordination number (CN).[‡] We see that a straight line fits the data quite well indicating an empirical dependence on the coordination number of $D/d \sim \sqrt{CN}$. The figure allows an estimate as to which atoms or molecules might be entrapped in a particular host material. From the figure, we can see that the group 14 clathrate-II E_{20} and E_{28} polyhedra fall in the intermediate range for this ratio, with the smallest and largest values in the figure being for the tetrahedron and the fullerene C_{60} , respectively.

The clathrate materials can also be considered as expanded forms of silicon, germanium, and tin, and as a result of their cage-like structure they can be considered as “naturally” nanoporous crystalline solids. As a consequence of their open structure, the volume per framework atom is as much as 15 to 20% larger in the clathrate relative to the diamond structure. However, the average E–E bond lengths for the guest-free Si_{136} (2.34 Å; Ref. 1) and Ge_{136} (2.45 Å; Ref. 2) clathrates are not significantly different from the “ideal” bond lengths for the corresponding diamond structures.⁷¹ In addition, the clathrate-II bond angles average close to the ideal 109.47° expected for

[‡] The free cavity diameter is derived by subtracting the cage member covalent diameter (*i.e.* the distance between cage member atoms) from twice the center to cage member distance. Thus it is a measure of the free “space” within the cage.

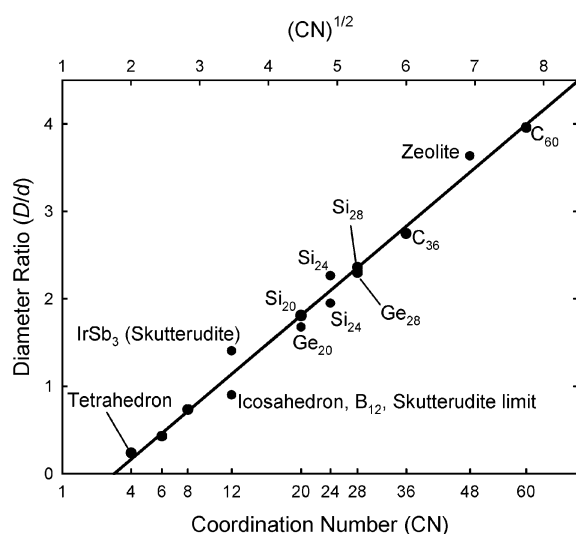


Fig. 2 Free cavity diameter to cage-member diameter ratio *versus* coordination number (CN) of the interior (*i.e.* guest) site, for several cage-like materials.³⁹ Si₂₄ corresponds to the “flattened” clathrate-I tetrakaidecahedra, which has two characteristic dimensions.

tetrahedral coordination. The effect of incorporation of guests into the structure results in a small but significant expansion of the structure.^{9,72–74}

The clathrate-II allotropes such as the empty Si₁₃₆ and Ge₁₃₆ are energetically metastable with respect to the diamond structured phases. However, the energy difference is apparently quite small,^{33,47,48} and a significant energy and/or kinetic barrier must exist allowing the clathrate structure to endure. San-Miguel *et al.*⁷⁵ and Ramachandran *et al.*⁷⁶ independently have shown that the Si₁₃₆ framework is stable under pressure up to 11 GPa. Moreover, no transition towards the diamond phase is observed, rather the Si₁₃₆ framework undergoes an irreversible transition to the β -Sn structure of silicon at 11.5 GPa, accompanied by a large volume reduction of more than 30%.^{75,76} Further discussion of the high pressure properties and stability of clathrates may be found in the literature.^{42,43,77,78}

Some of the most interesting structural aspects of clathrate-II materials are related to the relatively weak bonding between the guest atoms and the host framework. Nolas *et al.*⁷⁹ have reported on temperature dependent single crystal X-ray diffraction studies on several clathrate-II silicon and germanium compounds. Fig. 3 shows the temperature dependence of the isotropic atomic displacement parameters (ADP or U_{iso}) for the framework atoms in these compounds, as well as for the guest atoms inside the larger E₂₈ cage. For all of the guests, the ADPs are considerably larger than those of the framework sites. Moreover, there is much stronger temperature dependence for the guest ADPs relative to the framework. The magnitude and temperature dependence of the guest ADPs is indicative of relatively large amplitude thermal motion, and is a consequence of both the significant “space” inside the hexakaidecahedra, as well as relatively weak bonding between guest and framework. Bobev and Sevov⁹ have estimated the relative size of guest and cage by subtracting framework atom radii from the shortest guest–framework distances, compared to the ionic radii of the guests. It is interesting to note that in general the larger the difference in size between

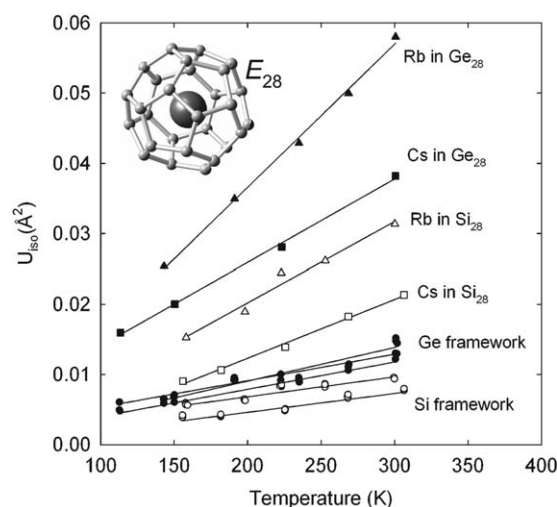


Fig. 3 Temperature dependent isotropic atomic displacement parameters (U_{iso}) for the E₂₈ guest as well as framework sites in A₈Na₁₆E₁₃₆ (A = Rb, Cs; E = Si, Ge).⁷⁹ The guest atoms all have significantly larger U_{iso} with stronger temperature dependence than those for the framework, with the U_{iso} increasing with decreasing guest size relative to its cage.

the guest relative to its E₂₈ cage, the larger the ADP, as evidenced in Fig. 3. The relationship of the guest motion to the thermal properties of these materials is discussed in more detail below.

Assuming the full $Fd\bar{3}m$ symmetry, the guest atoms in the clathrate-II structure are located at the centers of their respective polyhedral cages. However, in the case of the Na₄Si₁₃₆ clathrate it was originally suggested by Demkov *et al.*,⁴⁴ who used quantum molecular dynamics simulations, that the Na guest inside the Si₂₈ cage could in fact move off-center, thus lowering the site symmetry from T_d to C_{3v} . This was interpreted in terms of a Jahn–Teller distortion, and accompanying energy-lowering lifting of the degeneracy of the lowest conduction band.⁴⁴ Electron spin resonance measurements⁸⁰ reported soon after gave experimental evidence for this guest displacement in Na₃Si₁₃₆. More recently, analysis of extended X-ray absorption fine structure (EXAFS) measurements^{81,82} and accompanying theoretical studies indicate that the Na guests in the Si₂₈ polyhedra can indeed move off-center in the Na_xSi₁₃₆ clathrates ($x = 8$ and 24), toward the shared hexagonal faces by as much as 1 Å. Those results were interpreted in terms of the formation of a dimer between Na guests in adjacent Si₂₈ cages, shown schematically in Fig. 4. This effect may be akin to the well known Peierls distortion associated with the hypothetical one-dimensional monatomic lattice. As suggested by temperature dependent NMR data, a similar dimerization may also occur between Cs guests in Cs₈Ge₁₃₆.⁸³ The off-center nature of guest atoms in clathrate-I compounds such as Sr₈Ga₁₆Ge₃₀ and Eu₈Ga₁₆Ge₃₀ has been shown^{26,27,84–87} to be intimately linked to their unique physical properties, and such phenomena remain an aspect warranting further study in clathrate-II compounds.

Synthetic routes

There are various synthetic methods that have been used to prepare inorganic clathrate-II materials, and some compositions can be produced by more than one method. Arguably the most

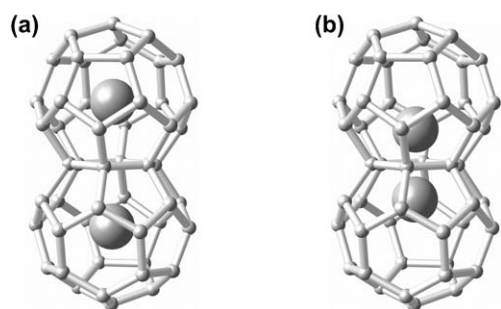


Fig. 4 Dimer formation between the Na guests in the $\text{Na}_x\text{Si}_{136}$ clathrates. (a) In the ideal $Fd\bar{3}m$ symmetry the guests occupy the centers of the Si_{28} polyhedra. (b) EXAFS measurements indicate the formation of a weak dimer between Na guests in adjacent Si_{28} cages, with the guests moving toward the shared hexagonal face of the polyhedra.^{81,82}

straightforward method is direct synthesis from the elements. Guided by the observation that stabilization of the clathrate-II structure is facilitated through matching relative sizes of guest and cage, Bobev and Sevov first synthesized^{9,72} the $\text{A}_8\text{Na}_{16}\text{E}_{136}$ clathrates ($\text{A} = \text{Cs}, \text{Rb}$; $\text{E} = \text{Si}, \text{Ge}$) by reaction of the high purity elements inside sealed niobium capsules. The mixtures were held at 650 °C for three weeks, and then slowly cooled to room temperature. Later, Nolas *et al.*^{79,88,89} used a similar method to synthesize these compounds for further characterization. The products were well-formed small crystals (~ 1 to 3 mm in size), typically along with coarse polycrystalline powders. An important consideration in the synthesis of these alkali-containing clathrates is the relatively high vapor pressure of the alkali metals and their ability to react easily with quartz ampoules if used, so that reactions must be carried out within sealed, metal vessels. The synthesis of a Sn clathrate-II compound has also been reported⁹⁰ by reaction of a mixture of $\text{K} : \text{Ba} : \text{Ga} : \text{Sn}$ in the ratio 8 : 16 : 32 : 104, with no K incorporated into the end compound $\text{Ba}_{16}\text{Ga}_{32}\text{Sn}_{104}$. This is the only Sn clathrate-II compound reported to date. Very recently, Beekman *et al.*⁹¹ have shown that $\text{Cs}_8\text{Na}_{16}\text{Ag}_x\text{Ge}_{136-x}$ compounds, with the framework Ge atoms substituted by Ag, can be synthesized by direct reaction of the elements. Bobev *et al.*⁹² have reported similar investigations of Ga substitution in Si clathrate-II compounds. The stability of group 14 clathrate-II materials under framework substitution introduces the opportunity to investigate new compositions within this structure type, allowing for the study of their physical properties. Semiconducting clathrate-II compounds in particular are expected to have promising thermoelectric properties.^{39–41,79}

New compositions may also be prepared from those synthesized directly from the elements. This follows from the fact that, in contrast to other group 14 clathrate structures, the guest concentration in the clathrate-II may be varied while still maintaining the integrity of the structure. Gryko *et al.*⁸³ have synthesized the clathrate $\text{Cs}_8\text{Ge}_{136}$, in which Cs occupies the larger Ge_{28} cages in the structure. This was achieved by first starting with stoichiometric $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$, prepared from the elements as discussed above. The Na content was then reduced by successively heating $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$ under high vacuum, causing the Na to “degas” from the clathrate, while Cs remained incorporated in the structure. Using this procedure, the Na content can be

reduced to less than 600 ppm. Similarly, $\text{Rb}_8\text{Ge}_{136}$ can also be prepared in this manner.⁹³

Although direct synthesis may be the most straightforward synthesis route, this method has to date been unsuccessful in synthesizing several compositions. Examples include the $\text{Na}_x\text{Si}_{136}$ ($0 < x < 24$) clathrates. These were of the first group 14 clathrates to be discovered by Kasper *et al.*,³ followed shortly thereafter by a systematic study originally undertaken by Cros *et al.*^{15–18} $\text{Na}_x\text{Si}_{136}$ are prepared *via* thermal decomposition of the Zintl compound NaSi.^{3,15–18,73,74,94} NaSi is prepared from the elements by reaction at 650 °C or higher under inert atmosphere, and the product is extremely air and moisture sensitive and handling must be performed in a N_2 or Ar glove-box. $\text{Na}_x\text{Si}_{136}$ is formed upon heating NaSi under vacuum ($< 10^{-5}$ torr) to temperatures above 350 °C. The structure of NaSi is monoclinic⁹⁵ (space group $C2/c$) and consists of Na^+ and $[\text{Si}_4]^{4-}$ Zintl ions (Fig. 5a).⁹⁶ During thermal decomposition, most of the Na^+ ions are reduced and are removed as vapor, with the remaining Na acting as a template for the Si_{136} framework formed by reconstruction of the $[\text{Si}_4]^{4-}$ cluster ions. The sodium content x is controlled by varying both the temperature and time for which the specimen is heated, with higher temperatures and longer times leading to lower sodium contents. The relative intensities of several reflections from powder X-ray diffraction exhibit a strong dependence upon the Na content,^{18,73,74} thus allowing the determination of the Na content from, for example, Rietveld structural refinement^{97,98} using powder diffraction data.^{73,74} The relative occupancy of the cages can also be determined in this way.^{73,74}

In addition to $\text{Na}_x\text{Si}_{136}$, the clathrate-I $\text{Na}_8\text{Si}_{46}$ is also commonly present in specimens prepared from decomposition of NaSi,^{73,74} sometimes in as much as 45 wt% in as prepared specimens.⁷³ This poses a challenge to producing $\text{Na}_x\text{Si}_{136}$ specimens of high purity for further characterization. Ramachandran *et al.*⁷³ have utilized the difference in densities between the two phases in order to separate them. However, this technique can be quite difficult to employ, as the crystallites of the two phases are often inter-grown.⁹⁹ The production of very high purity $\text{Na}_x\text{Si}_{136}$ specimens (*i.e.* with negligible $\text{Na}_8\text{Si}_{46}$ fraction) continues to be a challenge that must be addressed. This is necessary, for instance, to thoroughly characterize their electrical and thermal transport properties.

Unlike the case for $\text{Na}_x\text{Si}_{136}$, thermal decomposition of binary phases under vacuum is not as successful in producing the Ge analogue $\text{Na}_x\text{Ge}_{136}$ from NaGe. Although $\text{Na}_x\text{Ge}_{136}$ can be prepared from NaGe,⁴ a systematic study has shown that the yield is typically small, and $\text{Na}_x\text{Ge}_{136}$ only forms in a narrow range of synthesis temperatures.¹⁰⁰ Rather, the hexagonal

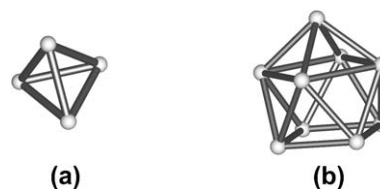


Fig. 5 Polyatomic Zintl anions (a) $[\text{E}_4]^{4-}$ and (b) $[\text{E}_9]^{4-}$ that act as precursor constituents in the synthesis of group 14 clathrate-II materials *via* thermal decomposition of silicides or germanides, as well as reaction in ionic liquids.

zeolite-like framework phase $\text{Na}_{1-x}\text{Ge}_{3+z}$ forms as the majority phase.¹⁰¹ The reason may be linked to the starting structures of the precursor compounds NaSi and NaGe: although both are monoclinic and are composed of Na^+ and $[\text{E}_4]^{4-}$ Zintl ions, the structures are not identical.⁹⁵ Thus the subtle morphological differences in NaGe (space group $P2_1/c$) and NaSi (space group $C2/c$) may promote differing structures for the decomposition products.

Other clathrate-II compositions have also been prepared by the thermal decomposition of mixed alkali or alkali-alkaline earth silicides. Ramachandran *et al.*¹⁰² synthesized $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$ by thermal decomposition of $\text{Cs}_x\text{Na}_{1-x}\text{Si}$, while similarly Lattur *et al.*¹⁰³ synthesized $\text{Rb}_8\text{Na}_{16}\text{Si}_{136}$ from $\text{Rb}_x\text{Na}_{1-x}\text{Si}$. The synthesis of $\text{Ba}_8\text{Na}_{16}\text{Si}_{136}$ via thermal decomposition of Na_2BaSi_4 has also been reported,¹⁰⁴ though the products consisted of a mixture of several phases. It is interesting to note that all precursors used thus far to prepare inorganic clathrates via thermal decomposition contain cluster $[\text{E}_4]^{4-}$ anions, an aspect clearly linked to their ability to produce the clathrate-II structure under decomposition.

One of the original questions concerning group 14 clathrate-II materials was the stability of the structure upon complete removal of the guests. Gryko *et al.*¹ showed that the clathrate-II structure is indeed stable when empty (Na content less than 600 ppm Si), and prepared the empty silicon clathrate Si_{136} by means of repeated degassing of $\text{Na}_x\text{Si}_{136}$ and treatment with concentrated acids. Ammar *et al.*¹⁰⁵ later also prepared Si_{136} using a similar technique, but reduced the residual Na content even further by reaction of the clathrates with iodine (final residual Na content ~ 35 ppm Si). The crystalline clathrate Si_{136} in essence constitutes a new allotrope of silicon.

Although preparing a guest-free Ge_{136} clathrate by the above described process of degassing $\text{Na}_x\text{Ge}_{136}$ is not feasible,^{100,101} an innovative technique has recently been developed by Guloy *et al.*² in order to circumvent this difficulty. These authors utilized the favorable properties of ionic liquids in polymerizing $[\text{Ge}_9]^{4-}$ (Fig. 5b) from solution in order to synthesize the guest-free clathrate. By dissolving a precursor of nominal composition Na_4Ge_9 in a 1 : 1 molar ratio melt of AlCl_3 and dodecyltrimethylammonium chloride (DTAC), and then heating the solution at

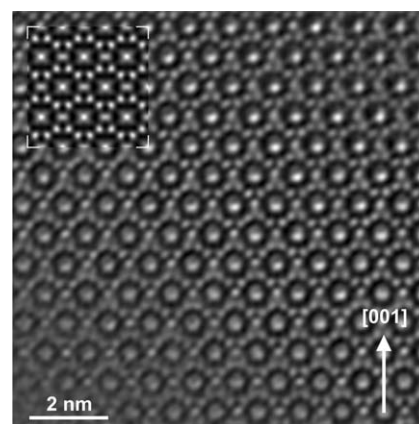
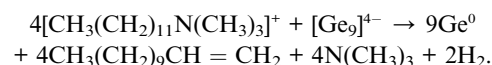


Fig. 6 High resolution transmission electron microscope (HRTEM) image of the new germanium allotrope Ge_{136} , taken for the $[110]$ zone axis. A simulated image is shown in the upper left-hand corner. Reprinted with permission from Ref. 2.

300°C while sealed under inert atmosphere, they were able to produce specimens with the majority phase being the guest-free clathrate Ge_{136} (see Fig. 6). This was explained in terms of the reaction of the $[\text{Ge}_9]^{4-}$ with DTAC according to²



This new open-structured allotrope¹⁰⁶ of Ge deserves further characterization. Using the same procedure, but with the precursor K_4Ge_9 , the authors also reported the synthesis of the clathrate-II $\text{K}_8\text{Ge}_{136}$.² This solution phase method utilizes the dissolved $[\text{E}_n]^{4-}$ cluster anions, analogous to the $[\text{E}_4]^{4-}$ anions found in the alkali metal silicides or germanides used in thermal decomposition. The presence of these Zintl ions in such precursors is clearly beneficial to the formation of the clathrate-II structure. Similar techniques have also recently been used to prepare mesoporous Ge by polymerization of $[\text{Ge}_9]^{4-}$ ions from solution, using potassium germanides as precursors.^{107,108}

Table 1 lists clathrate-II compositions that have been reported to date. Through a comparison with the inorganic clathrate-I

Table 1 Clathrate-II compositions, synthesis method, and lattice parameters

Composition	Synthesis method	Lattice parameter $a/\text{\AA}$	Reference ^a
Si_{136}	Degassing of $\text{Na}_x\text{Si}_{136}$	14.62601(9)	1
$\text{Na}_x\text{Si}_{136}$	Decomposition of NaSi	$14.62601(9) \leq a < 14.70704(1)$ ($0 \leq x < 24$)	1, 73
$\text{Cs}_7\text{Si}_{136}$	Decomposition of CsSi	14.64	4
$\text{Rb}_8\text{Na}_{16}\text{Si}_{136}$	Direct reaction of elements	14.7400(4)	9
$\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$	Direct reaction of elements	14.7560(4)	9
$\text{Ba}_8\text{Na}_{16}\text{Si}_{136}$	Decomposition of Na_2BaSi_4	Not reported	104
$\text{Rb}_{7.3}\text{Na}_{16}\text{Ga}_{20}\text{Si}_{116}$	Direct reaction of elements	14.883(2)	92
$\text{Cs}_8\text{Na}_{16}\text{Ga}_{21}\text{Si}_{115}$	Direct reaction of elements	14.918(2)	92
Ge_{136}	Reaction of $[\text{Ge}_9]^{4-}$ in DTAC- AlCl_3	15.2115(1)	2
$\text{Na}_x\text{Ge}_{136}$	Decomposition of NaGe	15.4	4
$\text{Cs}_8\text{Ge}_{136}$	Degassing of $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$	15.329	83
$\text{Rb}_8\text{Na}_{16}\text{Ge}_{136}$	Direct reaction of elements	15.4858(6)	9
$\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$	Direct reaction of elements	15.4805(6)	9
$\text{Cs}_8\text{Na}_{16}\text{Ag}_{6.7}\text{Ge}_{129.3}$	Direct reaction of elements	15.51618(9)	91
$\text{Ba}_{16}\text{Ga}_{32}\text{Sn}_{104}$	Direct reaction of elements	17.054(1)	90

^a Selected references.

materials, we can see that the possible clathrate-II compositions still to be investigated are significant. The synthesis of new compositions, in addition to those listed in Table 1, is important for the study of their physical and chemical properties, and to develop a fundamental understanding of structure–property relationships in open-framework and guest–host materials of group 14 elements. Some of the progress thus far toward this understanding is outlined in the remainder of the article.

Electronic properties

Since the observation of unique optical properties in porous silicon,¹⁰⁹ low-density forms of this technologically important semiconductor have continued to be investigated for their interesting electronic properties, in comparison to the bulk crystalline diamond structured state. An important discovery regarding the electronic properties of clathrate-II materials was the theoretical prediction³³ and later experimental verification¹ that the band gap of the empty clathrate Si_{136} is expanded by approximately 0.7 eV relative to that for diamond structured silicon (E_{gap} of diamond Si \approx 1.1 eV). Thus the Si_{136} allotrope constitutes a wide band gap semiconductor. However, whereas the interesting optical properties of materials such as porous silicon have been attributed to quantum confinement effects, the opening of the gap in Si_{136} (relative to diamond structured Si) can be understood in terms of the slight distortion in the clathrate of the ideal tetrahedral bonding found in diamond-state silicon, as well as the high density of 5-membered rings in the Si_{136} structure.³³ Recent theoretical work³⁶ has discussed the importance of symmetry considerations for the optical properties of silicon clathrate-II materials, as well as the potential for intercalation of guests with electronegativities that are higher than that of silicon.

A promising aspect of these open-framework Si and Ge semiconductors is the potential for band gap engineering with composition. Moriguchi *et al.*³⁴ have explored the electronic structure of clathrate-II silicon–germanium alloys, $\text{Si}_{136-x}\text{Ge}_x$, using density functional techniques. These authors found that the effect of alloying silicon and germanium on the clathrate framework can not only allow for varying the ~ 2 eV band gap of Si_{136} , but also that $\text{Si}_{136-x}\text{Ge}_x$ clathrates should possess a direct band gap for a range of values of x . Their results indicate the band gap of $\text{Si}_{136-x}\text{Ge}_x$ alloys could be continuously “tuned” from approximately 1.2 to 2 eV, in the visible range of the electromagnetic spectrum. This band gap dependence can be contrasted to that observed in the diamond structured $\text{Si}_{1-x}\text{Ge}_x$ alloys (0.7 to 1.1 eV). Although the synthesis of $\text{Si}_{136-x}\text{Ge}_x$ clathrates has yet to be achieved, such properties make these materials of interest for potential use in optoelectronic or photovoltaic applications.

The electronic properties of the filled group 14 clathrates can be discussed in terms of a rigid band model, in which the electro-positive guests donate their valence electrons to the host framework. Within this model, the “empty” clathrate framework electronic band structure (*e.g.* that of Si_{136} or Ge_{136}) is only minimally modified by introduction of the guests into the framework cages, and the donated electrons occupy the framework conduction band levels. For compounds such as $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$ and $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$, the result is a high density of charge carriers ($>10^{21} \text{ cm}^{-3}$) and metallic properties. This is exemplified in Fig. 7, which shows results from temperature dependent

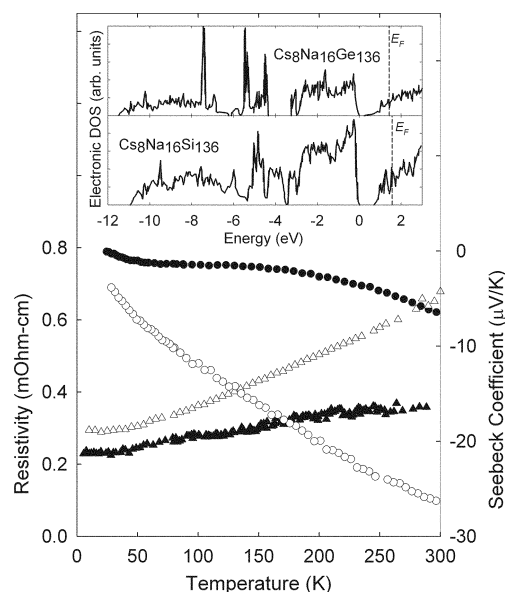


Fig. 7 Seebeck coefficient (round symbols) and resistivity (triangular symbols) as a function of temperature for polycrystalline $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$ (open symbols) and $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$ (filled symbols).⁷⁹ Inset: DFT computed electronic density of states for $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$ (lower)¹⁰² and $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$ (upper)⁸³; the dashed line indicates the Fermi level, which is well within the conduction band for both materials.

electrical transport measurements,⁷⁹ corroborated by calculations^{83,102} of the electronic density of states (DOS) for these two compounds. For both compounds, the resistivities increase monotonically with temperature (typical metallic behavior), while the Seebeck coefficients remain relatively small, the (negative) sign indicating electrons are the majority carriers. It should be noted that the rigid band approximation is, strictly speaking, a simplified model, and there is evidence that the introduction of the guests does indeed modify the band structure of these materials.¹¹⁰ Nevertheless, it remains a useful model for the qualitative understanding of the electronic properties of these materials. To date, the only semiconducting clathrate-II phases for which electrical transport properties have been reported are the guest-free Si_{136} and Ge_{136} , and the lower Na content $\text{Na}_x\text{Si}_{136}$. However, the ability to substitute other species for the framework atoms discussed above^{91,92} may allow the synthesis and characterization of new semiconducting clathrate-II variants.

The ability to adjust the guest content in clathrate-II materials offers a unique opportunity to study the effects of guest content and type on the physical properties of inorganic clathrates. It has been observed that the electrical properties of $\text{Na}_x\text{Si}_{136}$ ($0 < x < 24$) clathrates depend strongly on the Na content, in that increasing the guest content considerably reduces the electrical resistivity.^{4,111} In addition, high Na content $\text{Na}_x\text{Si}_{136}$ specimens exhibit metallic behavior whereas lower Na content specimens show semiconducting or insulating behavior.^{4,111,112} Transport,^{4,112} NMR,¹¹³ and magnetic susceptibility measurements,^{4,114} as well as theoretical calculations,^{44,110} indicate a metal insulator transition occurs at $7 < x < 12$, though the precise value of x at which this occurs has yet to be determined unequivocally and could also conceivably depend on the relative occupation of the two different caged sites in the structure. In analogy with the superconducting

fullerenes¹¹⁵ and also some clathrate-I compounds,^{20,21} the possibility of superconductivity in clathrate-II $\text{Na}_x\text{Si}_{136}$ ¹¹⁴ and $\text{Ba}_8\text{Na}_{16}\text{Si}_{136}$ ¹⁰⁴ has been explored, but with negative results.

The electronic structure of several clathrate-II phases has been studied employing nuclear magnetic resonance techniques.^{1,83,102,103,113,116–119} One feature common to several clathrate-II materials is the relatively large NMR shifts for both the guest and framework species. These shifts have been interpreted as akin to the Knight shifts in metals, originating in the hyperfine interactions between the NMR nuclei and the delocalized conduction electrons.¹²⁰ Indeed, the Knight shifts for ^{23}Na in the $\text{Na}_x\text{Si}_{136}$ clathrates (1600 to 2000 ppm as referenced to 1 mol NaCl at 0 ppm) are larger than in metallic sodium (1123 ppm).^{117–119} Moreover, in contrast to the behavior associated with Knight shifts in metals, which are typically found to be approximately temperature independent,¹²⁰ the Knight shifts in $\text{Rb}_8\text{Na}_{16}\text{Si}_{136}$,¹⁰³ $\text{Na}_x\text{Si}_{136}$,¹¹⁸ and $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$ ⁸³ are found to exhibit strong temperature dependences, increasing as the temperature is decreased. As originally suggested by Gryko *et al.*,¹¹⁸ this phenomenon appears to be related to distinct structural features in the electronic density of states near the Fermi level of these materials.^{61,118}

Thermal and vibrational properties

Of the most conspicuous aspects of inorganic clathrates are their thermal, lattice dynamical, and vibrational properties, which continue to be intensively studied.^{19,48,49,57,79,121–129} The relatively large number of atoms in the clathrate-II unit cell, as well as the presence or absence of the guests, results in distinctive thermal properties for these materials. As discussed above, the relatively large difference in size and weak bonding between guest and cage in many filled clathrates promotes localized guest vibration modes, a phenomenon which has been termed as “rattling.” This effect is observed in the magnitude and temperature dependence of the guest atom ADPs determined from single crystal XRD, as discussed above (Fig. 3).⁷⁹

Previous studies have shown^{130–132} that ADPs determined from crystallographic analysis can be used to estimate the frequencies of the localized vibrations undergone by guest atoms such as those in the clathrate-II materials, and also to estimate other pertinent physical quantities for the solid. With the assumption that the guest acts as a three dimensional “Einstein” oscillator,¹³³ the “rattler” frequency can be estimated from the simple relation $U_{\text{iso}} = k_{\text{B}}T/m(2\pi\nu)^2$, where k_{B} is Boltzmann’s constant, m is the mass of the “rattler”, and ν is the frequency of vibration. Vibration frequencies determined using this approach for $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$ and $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$ are given in Table 2.⁷⁹

Table 2 Vibrational frequencies in cm^{-1} for the guest atoms in $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$ and $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$, as determined from temperature dependent single crystal XRD (ADP data),⁷⁹ Raman scattering,⁸⁸ and density functional theory calculations^{57,88}

Compound	ν_{ADP}^{79}		ν_{Raman}^{88}		$\nu_{\text{theory}}^{57,88}$	
	Cs	Na	Cs	Na	Cs	Na
$\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$	53.4	141	57	Not active	64	120
$\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$	41.8	117	18	Not active	21	89

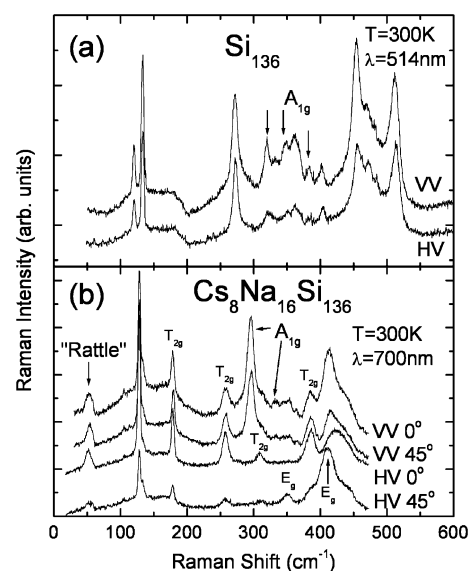


Fig. 8 Stokes Raman scattering spectra for Si_{136} and $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$.⁸⁸ The Cs “rattle” mode at $\sim 57 \text{ cm}^{-1}$ is indicated. Reprinted with permission from G. S. Nolas, C. A. Kendziora, J. Gryko, J. J. Dong, C. W. Myles, A. Poddar, and O. F. Sankey, *J. Appl. Phys.*, 2002, **92**, 7225.⁸⁸ Copyright 2002, American Institute of Physics.

The “rattling” motions of the guest atoms, or soft phonon modes, in the $\text{A}_8\text{B}_{16}\text{E}_{136}$ clathrates have also been observed using Raman scattering experiments.⁸⁸ From group theoretic analysis, it is found that the guest atoms in the larger E_{28} hexakaidecahedra contribute a Raman-active optic mode (T_{2g} symmetry), while the guest atoms in the smaller E_{20} dodecahedra do not contribute any Raman-active modes. Fig. 8 shows the room temperature Raman scattering spectra obtained on polycrystalline Si_{136} and single-crystal $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$. The low-frequency Cs “rattle” mode at 57 cm^{-1} is clearly discernable, and this observed Raman shift is in agreement with the frequency of 64 cm^{-1} predicted for this mode by density functional theory computations. A similar Cs optic mode was observed for $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$, and the majority of the other Raman-active vibrational modes, largely due to framework optical phonons, for Si_{136} , $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$, and $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$ were also identified.⁸⁸ A comparison of the guest vibration frequencies determined from the ADPs, Raman scattering, and theoretical calculations is given in Table 2.

Further theoretical calculations concerning the vibrational properties of filled $\text{A}_8\text{B}_{16}\text{E}_{136}$ clathrates have been reported by Myles *et al.*,⁵⁷ who used density functional techniques. Fig. 9 shows the calculated phonon dispersion curves for one of the compounds studied in that work, $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$. For the most part, the phonon dispersion is very similar in character to that calculated for the parent Ge_{136} clathrate.⁴⁸ The important difference, however, is the appearance of flat, nearly dispersionless modes corresponding to the localized motion of the Na and Cs guests (labeled in Fig. 9). In particular, the Cs guest modes are found well within the frequency range of the host acoustic phonons, which are responsible for the dominant heat carrying contribution to the lattice thermal conductivity.

The above results indicate the possibility for strong scattering of these acoustic phonons. Similar phenomena have been

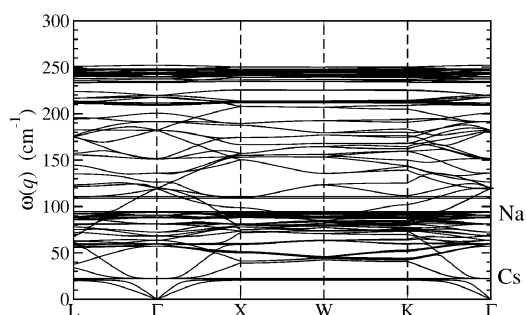


Fig. 9 Computed phonon dispersion relations along selected directions in reciprocal space for $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$.⁵⁷ The Na and Cs “rattle” modes are labeled. The frequency of the Cs mode is well within the range of the host Ge_{136} framework acoustic modes. Reprinted with permission from Ref. 57.

observed in group 14 clathrate-I materials¹⁹ as well as clathrate-II hydrates,¹³⁴ where localized guest vibrational modes can efficiently scatter heat-carrying acoustic phonons, resulting in dramatically reduced thermal conductivities. Recent experimental results¹¹¹ from thermal conductivity measurements on polycrystalline $\text{Na}_x\text{Si}_{136}$ specimens suggest this resonant scattering effect may indeed be present in some semiconducting clathrate-II variants; a detailed investigation into the transport properties of $\text{Na}_x\text{Si}_{136}$ clathrates is currently underway by the authors. We note that although there is clear evidence for the localized guest mode in materials such as $\text{Cs}_8\text{Na}_{16}\text{Ge}_{136}$ or $\text{Cs}_8\text{Na}_{16}\text{Si}_{136}$,^{57,79,88} the thermal conductivity appears to be dominated by the electronic component in these metallic compounds.^{79,135} The synthesis of new filled semiconducting clathrate-II variants will allow further study of their expected interesting thermal transport properties.

In addition to vibrational and thermal transport phenomena related to the caged guest motion, the open-structured framework of clathrate-II phases results in unique thermal properties in their own right. Nolas *et al.*¹²⁸ reported on the thermal properties of the empty clathrate Si_{136} , and found that this material has a very low thermal conductivity, an order of magnitude lower than that of diamond-structure silicon and comparable in magnitude with amorphous SiO_2 . This is observed even in the absence of the phonon scattering mechanisms found in filled clathrates.¹⁹ The low thermal conductivity of Si_{136} relative to diamond silicon can be understood in terms of the combined increase in unit cell size^{136,137} and open-framework structure of the former with respect to the latter. The results of theoretical studies^{123,137} point to distinct features in the phonon structure which are related to the relative increase in unit cell size. These include gaps in the phonon dispersion relations as well as zone-boundary folding, to which the very low thermal conductivity in the Si_{136} allotrope can be attributed. These results suggest additional approaches to the design of low thermal conductivity crystalline solids.

Concluding remarks

We have discussed current progress in understanding the structural and physical properties of the clathrate-II inorganic materials of group 14, as well as the diverse synthetic routes employed

to prepare them. New synthetic techniques are currently being explored in the effort to produce new compositions within this structure type, offering rich possibilities for further study of their unique properties. In particular, the ability to continuously vary the guest content and/or framework composition in these materials allows tuning of the electrical and thermal transport properties, of interest for potential applications in technologies such as thermoelectrics and optoelectronics. Inorganic clathrate-II phases are an emerging class of open-framework and guest–host materials that offer an opportunity to study unique physical phenomena in the solid state.

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References

- 1 J. Gryko, P. F. McMillan, R. F. Marzke, G. K. Ramachandran, D. Patton, S. K. Deb and O. F. Sankey, *Phys. Rev. B*, 2000, **62**, R7707.
- 2 A. M. Guloy, R. Ramlau, Z. Tang, W. Schnelle, M. Baitinger and Yu. Grin, *Nature*, 2006, **443**, 320.
- 3 J. S. Kasper, P. Hagenmuller, M. Pouchard and C. Cros, *Science*, 1965, **150**, 1713.
- 4 C. Cros, M. Pouchard and P. Hagenmuller, *J. Solid State Chem.*, 1970, **2**, 570.
- 5 J.-T. Zhao and J. D. Corbett, *Inorg. Chem.*, 1994, **33**, 5721.
- 6 H. Fukuoka, K. Iwai, S. Yamanaka, H. Abe, K. Yoza and L. Häming, *J. Solid State Chem.*, 2000, **151**, 117.
- 7 B. Eisenmann, H. Schafer and R. Zagler, *J. Less-Common Met.*, 1986, **118**, 43.
- 8 G. Cordier and P. Woll, *J. Less-Common Met.*, 1991, **169**, 291.
- 9 S. Bobev and S. C. Sevov, *J. Solid State Chem.*, 2000, **153**, 92.
- 10 J. Martin, S. Erickson, G. S. Nolas, P. Alboni, T. M. Tritt and J. Yang, *J. Appl. Phys.*, 2006, **99**, 044903.
- 11 S. Lattner, X. Bu, N. Blake, H. Metiu and G. Stucky, *J. Solid State Chem.*, 2000, **151**, 61.
- 12 G. A. Jeffrey, in *Inclusion Compounds*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, Academic Press, London, 1984, vol. 1, pp. 135–190.
- 13 W. L. Mao, C. S. Koh and E. D. Sloan, *Phys. Today*, 2007, **60**, 42.
- 14 E. D. Sloan and C. A. Koh, *Clathrate Hydrates of Natural Gases*, CRC Press/Taylor & Francis, Boca Raton, FL, 2007.
- 15 C. Cros, M. Pouchard and P. Hagenmuller, *C. R. Hebd. Seances Acad. Sci.*, 1965, **260**, 4764.
- 16 C. Cros, M. Pouchard and P. Hagenmuller, *Bull. Soc. Chim. Fr.*, 1971, 379.
- 17 C. Cros, M. Pouchard, P. Hagenmuller and J. S. Kasper, *Bull. Soc. Chim. Fr.*, 1968, 2737.
- 18 C. Cros and J.-C. Benejat, *Bull. Soc. Chim. Fr.*, 1972, 1739.
- 19 J. L. Cohn, G. S. Nolas, V. Fessatidis, T. H. Metcalf and G. S. Slack, *Phys. Rev. Lett.*, 1999, **82**, 779.
- 20 H. Kawaji, H.-O. Horie, S. Yamanaka and M. Ishikawa, *Phys. Rev. Lett.*, 1995, **74**, 1427.
- 21 S. Yamanaka, E. Enishi, H. Fukuoka and M. Yasukawa, *Inorg. Chem.*, 2000, **39**, 56.
- 22 S. Paschen, W. Carrillo-Cabrera, A. Bentien, V. H. Tran, M. Baenitz, Yu. Grin and F. Steglich, *Phys. Rev. B*, 2001, **64**, 214404.
- 23 G. T. Woods, J. Martin, M. Beekman, R. P. Hermann, F. Grandjean, V. Keppens, O. Leupold, G. J. Long and G. S. Nolas, *Phys. Rev. B*, 2006, **73**, 174403.

- 24 S. Srinath, J. Gass, J. Rebar, G. T. Woods, H. Srikanth and G. S. Nolas, *J. Appl. Phys.*, 2006, **99**, 08K902.
- 25 T. Kawaguchi, K. Tanigaki and M. Yasukawa, *Appl. Phys. Lett.*, 2000, **77**, 3438.
- 26 R. P. Hermann, V. Keppens, P. Bonville, G. S. Nolas, F. Grandjean, G. J. Long, H. M. Christen, B. C. Chakoumakos, B. C. Sales and D. Mandrus, *Phys. Rev. Lett.*, 2006, **97**, 17401.
- 27 I. Zerec, V. Keppens, M. A. McGuire, D. Mandrus, B. C. Sales and P. Thalmeier, *Phys. Rev. Lett.*, 2004, **92**, 185502.
- 28 W. Gou, Y. Li, J. Chi, J. H. Ross, Jr., M. Beekman and G. S. Nolas, *Phys. Rev. B*, 2005, **71**, 174307.
- 29 G. A. Slack, *Mater. Res. Soc. Symp. Proc.*, 1997, **478**, 47.
- 30 G. S. Nolas, J. L. Cohn, G. A. Slack and S. B. Schujman, *Appl. Phys. Lett.*, 1998, **73**, 178.
- 31 A. Saramat, G. Svensson, A. E. C. Palmqvist, C. Stiewe, E. Mueller, D. Platzek, S. G. K. Williams, D. M. Rowe, J. D. Bryan and G. D. Stucky, *J. Appl. Phys.*, 2006, **99**, 23708.
- 32 J.-H. Kim, N. L. Okamoto, K. Kishida, K. Tanaka and H. Inui, *Acta Mater.*, 2006, **54**, 2057.
- 33 G. B. Adams, M. O'Keefe, A. A. Demkov, O. F. Sankey and Y.-M. Huang, *Phys. Rev. B*, 1994, **49**, 8048.
- 34 K. Moriguchi, S. Munetoh and A. Shintani, *Phys. Rev. B*, 2000, **62**, 7138.
- 35 J. C. Conesa, C. Tablero and P. Wahnón, *J. Chem. Phys.*, 2004, **120**, 6142.
- 36 D. Connétable, *Phys. Rev. B*, 2007, **75**, 125202.
- 37 X. Blase, P. Gillet, A. San Miguel and P. Mélinon, *Phys. Rev. Lett.*, 2004, **92**, 215505.
- 38 P. Rogl, in *Thermoelectrics Handbook: Macro to Nano*, ed. D. M. Rowe, CRC Press, Boca Raton, 2006, p. 32-1.
- 39 G. S. Nolas, G. A. Slack and S. B. Schujman, in *Semiconductors and Semimetals*, ed. T. M. Tritt, Academic Press, San Diego, 2000, vol. 69, p. 255.
- 40 G. S. Nolas, in *Chemistry, Physics, and Materials Science of Thermoelectric Material: Beyond Bismuth Telluride*, ed. M. G. Kanatzidis, S. D. Manthani, and T. P. Hogan, Kluwer Academic/Plenum Publishers, New York, 2003, pp. 107-120.
- 41 G. S. Nolas, in *Thermoelectrics Handbook: Macro to Nano*, ed. D. M. Rowe, CRC Press, Boca Raton, 2006, p. 33-1.
- 42 A. San-Miguel and P. Toulemonde, *High Pressure Res.*, 2005, **25**, 159.
- 43 P. Toulemonde, A. San-Miguel, A. Merlen, R. Viennois, S. Le Floch, Ch. Adessi, X. Blase and J. L. Tholence, *J. Phys. Chem. Solids*, 2006, **67**, 1117.
- 44 A. A. Demkov, O. F. Sankey, K. E. Schmidt, G. B. Adams and M. O'Keefe, *Phys. Rev. B*, 1994, **50**, 017001.
- 45 M. Menon, E. Richter and K. R. Subbaswamy, *Phys. Rev. B*, 1997, **56**, 12290.
- 46 D. Kahn and J. P. Lu, *Phys. Rev. B*, 1997, **56**, 13898.
- 47 M. O'Keefe, G. B. Adams and O. F. Sankey, *Philos. Mag. Lett.*, 1998, **78**, 21.
- 48 J. J. Dong and O. F. Sankey, *J. Phys.: Condens. Matter*, 1999, **11**, 6129.
- 49 J. J. Dong, O. F. Sankey and G. Kern, *Phys. Rev. B*, 1999, **60**, 950.
- 50 S. Munetoh, K. Moriguchi, K. Kamei, A. Shintani and T. Motooka, *Phys. Rev. Lett.*, 2001, **86**, 4879.
- 51 K. Moriguchi, S. Munetoh, A. Shintani and T. Motooka, *Phys. Rev. B*, 2001, **64**, 195409.
- 52 J. S. Tse, K. Uehara, R. Rousseau, A. Ker, C. I. Ratcliffe, M. A. White and G. MacKay, *Phys. Rev. Lett.*, 2000, **85**, 114; J. S. Tse, K. Uehara, R. Rousseau, A. Ker, C. I. Ratcliffe, M. A. White and G. MacKay, *Phys. Rev. Lett.*, 2001, **86**, 4980 (erratum).
- 53 W. Sekkal, A. Zaoui and S. A. Abderrahmane, *Mater. Sci. Eng., B*, 2003, **97**, 176.
- 54 X. Blase, *Phys. Rev. B*, 2003, **67**, 35211.
- 55 H. Libotte, J. P. Gaspard, A. San Miguel and P. Melinon, *Europhys. Lett.*, 2003, **64**, 757.
- 56 M. Wilson and P. F. McMillan, *Phys. Rev. Lett.*, 2003, **90**, 13703.
- 57 C. W. Myles, J. J. Dong and O. F. Sankey, *Phys. Status Solidi B*, 2003, **239**, 26.
- 58 H. Libotte and J. P. Gaspard, *High Pressure Res.*, 2004, **24**, 139.
- 59 M. Kaczmarzki, O. N. Bedoya-Martínez and E. R. Hernández, *Phys. Rev. Lett.*, 2005, **94**, 95701.
- 60 D. S. Krupskii, O. S. Subbotin and V. R. Belosludov, *Comput. Mater. Sci.*, 2006, **36**, 225.
- 61 K. Biswas and C. W. Myles, *Phys. Rev. B*, 2006, **74**, 115113.
- 62 K. Biswas and C. W. Myles, *Phys. Rev. B*, 2007, **75**, 245205.
- 63 C. R. Miranda and A. Antonelli, *Phys. Rev. B*, 2006, **74**, 153203.
- 64 W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*, 1990, **347**, 354.
- 65 M. T. Lin and M. L. Cohen, *Phys. Rev. B*, 1984, **29**, 6996.
- 66 M. S. Dresselhaus, G. Dresselhaus and P. C. Ecklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego, 1996.
- 67 P. Mélinon, P. Kéghélian, X. Blase, J. Le Brusq, A. Perez, E. Reny, C. Cros and M. Pouchard, *Phys. Rev. B*, 1998, **58**, 12590.
- 68 M. Pouchard, C. Cros, P. Hagenmüller, E. Reny, A. Ammar, M. Menetrier and J. M. Bassat, *Solid State Sci.*, 2002, **4**, 723.
- 69 S. Alvarez, *Dalton Trans.*, 2005, 2209.
- 70 S. Alvarez, *Dalton Trans.*, 2006, 2045.
- 71 N. A. Goryunova, *The Chemistry of Diamond-like Semiconductors*, MIT Press, Cambridge, 1963.
- 72 S. Bobev and S. C. Sevov, *J. Am. Chem. Soc.*, 1999, **121**, 3796.
- 73 G. K. Ramachandran, J. J. Dong, J. Diefenbacher, J. Gryko, R. F. Marzke, O. F. Sankey and P. F. McMillan, *J. Solid State Chem.*, 1999, **145**, 716.
- 74 E. Reny, P. Gravereau, C. Cros and M. Pouchard, *J. Mater. Chem.*, 1998, **8**, 2839.
- 75 A. San-Miguel, P. Kéghélian, X. Blase, P. Mélinon, A. Perez, J. P. Itié, A. Polian, E. Reny, C. Cros and M. Pouchard, *Phys. Rev. Lett.*, 1999, **83**, 5290.
- 76 G. K. Ramachandran, P. F. McMillan, S. K. Deb, M. Somayazulu, J. Gryko, J. J. Dong and O. F. Sankey, *J. Phys.: Condens. Matter*, 2000, **12**, 4013.
- 77 P. F. McMillan, *Nat. Mater.*, 2002, **1**, 19.
- 78 A. San-Miguel, *Chem. Soc. Rev.*, 2006, **35**, 876.
- 79 G. S. Nolas, D. G. Vanderveer, A. P. Wilkinson and J. L. Cohn, *J. Appl. Phys.*, 2002, **91**, 8970.
- 80 H. Yabiro, K. Yamaji, M. Shiotani, S. Yamanaka and M. Ishikawa, *Chem. Phys. Lett.*, 1995, **246**, 167.
- 81 F. Brunet, P. Mélinon, A. San-Miguel, P. Kéghélian, A. Perez, A. M. Flank, E. Reny, C. Cros and M. Pouchard, *Phys. Rev. B*, 2000, **61**, 16550.
- 82 F. Tournus, B. Masenelli, P. Mélinon, D. Connétable, X. Blase, A. M. Flank, P. Lagarde, C. Cros and M. Pouchard, *Phys. Rev. B*, 2004, **69**, 035208.
- 83 J. Gryko, R. F. Marzke, G. A. Lamberton, Jr., T. M. Tritt, M. Beekman and G. S. Nolas, *Phys. Rev. B*, 2005, **71**, 115208.
- 84 G. S. Nolas, T. J. R. Weakley, J. L. Cohn and R. Sharma, *Phys. Rev. B*, 2000, **61**, 3845.
- 85 B. C. Chakoumakos, B. C. Sales, D. G. Mandrus and G. S. Nolas, *J. Alloys Compd.*, 2000, **296**, 80.
- 86 F. Bridges and L. Downward, *Phys. Rev. B*, 2004, **70**, 140201R.
- 87 R. Baumbach, F. Bridges, L. Downward, D. Cao, P. Chesler and B. Sales, *Phys. Rev. B*, 2005, **71**, 024202.
- 88 G. S. Nolas, C. A. Kendziora, J. Gryko, J. J. Dong, C. W. Myles, A. Poddar and O. F. Sankey, *J. Appl. Phys.*, 2002, **92**, 7225.
- 89 J. A. Kaduk, W. Wong-Ng and G. S. Nolas, *Rigaku J.*, 2003, **20**, 2.
- 90 R. Kröner, K. Peters, H. G. von Schnering and R. Nesper, *Z. Kristallogr. – New Cryst. Struct.*, 1998, **213**, 664.
- 91 M. Beekman, W. Wong-Ng, J. A. Kaduk, A. Shapiro and G. S. Nolas, *J. Solid State Chem.*, 2007, **180**, 1086.
- 92 S. Bobev, J. Meyers, Jr., V. Fritsch and Y. Yamasaki, *Proc. Int. Conf. Thermoelectr.*, 2006, **25**, 48.
- 93 J. Gryko, M. Beekman and G. S. Nolas, unpublished results.
- 94 J. Gryko, U.S. Patent No. 6 423 286.
- 95 R. Schäfer and W. Klemm, *Z. Anorg. Allg. Chem.*, 1961, **312**, 214.
- 96 *Chemistry, Structure and Bonding of Zintl Phases and Ions*, ed. S. M. Kauzlarich, VCH, New York, 1996.
- 97 H. M. Rietveld, *Acta Crystallogr.*, 1967, **22**, 151.
- 98 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65.
- 99 J. Gryko, personal communication; M. Beekman and G. S. Nolas, unpublished results.
- 100 M. Beekman, J. Gryko, H. F. Rubin, J. A. Kaduk, W. Wong-Ng and G. S. Nolas, *Proc. Int. Conf. Thermoelectr.*, 2005, **24**, 219.
- 101 M. Beekman, J. A. Kaduk, Q. Huang, W. Wong-Ng, W. Yang, D. Wang and G. S. Nolas, *Chem. Commun.*, 2007, 837.
- 102 G. K. Ramachandran, J. J. Dong, O. F. Sankey and P. F. McMillan, *Phys. Rev. B*, 2000, **63**, 033102.
- 103 S. Lattur, B. B. Iverson, J. Sepa, V. Srdanov and G. Stucky, *Phys. Rev. B*, 2001, **63**, 12543.

- 104 T. Rachi, K. Tanigaki, R. Kumashiro, J. Winter and H. Kuzmany, *Chem. Phys. Lett.*, 2005, **409**, 48.
- 105 A. Ammar, C. Cros, M. Pouchard, N. Jaussaud, J.-M. Bassat, G. Villeneuve, M. Duttine, M. Ménétrier and E. Reny, *Solid State Sci.*, 2004, **6**, 393.
- 106 T. F. Fassler, *Angew. Chem., Int. Ed.*, 2007, **46**, 2572.
- 107 G. S. Armatas and M. C. Kanatzidis, *Science*, 2006, **313**, 817.
- 108 D. Sun, A. E. Riley, A. J. Cadby, E. K. Richman, S. D. Korlann and S. H. Tolbert, *Nature*, 2006, **441**, 29.
- 109 L. T. Canham, *Appl. Phys. Lett.*, 1990, **57**, 1046.
- 110 V. I. Smelyansky and J. S. Tse, *Chem. Phys. Lett.*, 1997, **264**, 459.
- 111 M. Beekman and G. S. Nolas, *Physica B*, 2006, **383**, 111.
- 112 N. F. Mott, *J. Solid State Chem.*, 1973, **6**, 348.
- 113 E. Reny, M. Ménétrier, C. Cros, M. Pouchard and J. S n gas, *C. R. Acad. Sci., Ser. IIC: Chim.*, 1998, **1**, 129.
- 114 S. B. Roy, K. E. Sim and A. D. Caplan, *Philos. Mag. B*, 1992, **65**, 1445.
- 115 A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan, *Nature*, 1991, **350**, 600.
- 116 F. Shimizu, Y. Maniwa, K. Kume, H. Kawaji, S. Yamanka and M. Ishikawa, *Synth. Met.*, 1997, **86**, 2141.
- 117 J. Gryko, P. F. McMillan and O. F. Sankey, *Phys. Rev. B*, 1996, **54**, 3037.
- 118 J. Gryko, P. F. McMillan, R. F. Marzke, A. P. Dodokin, A. A. Demkov and O. F. Sankey, *Phys. Rev. B*, 1998, **57**, 4172.
- 119 J. He, D. D. Klug, K. Uehara, K. F. Preston, C. I. Ratcliffe and J. S. Tse, *J. Phys. Chem. B*, 2001, **105**, 3475.
- 120 C. P. Slichter, *Principles of Magnetic Resonance*, Harper and Row, New York, 1963.
- 121 Y. Guyot, B. Champagnon, E. Reny, C. Cros, M. Pouchard, P. Melinon, A. Perez and I. Gregora, *Phys. Rev. B*, 1998, **57**, R9475.
- 122 Y. Guyot, L. Grosvalet, B. Champagnon, E. Reny, C. Cros and M. Pouchard, *Phys. Rev. B*, 1999, **60**, 14507.
- 123 J. J. Dong, O. F. Sankey and C. W. Myles, *Phys. Rev. Lett.*, 2001, **86**, 2361.
- 124 B. C. Sales, B. C. Chakoumakos, R. Jin, J. R. Thompson and D. Mandrus, *Phys. Rev. B*, 2001, **63**, 245113.
- 125 A. Bentien, M. Christensen, J. D. Bryan, A. Sanchez, S. Paschen, F. Steglich, G. D. Stucky and B. B. Iversen, *Phys. Rev. B*, 2004, **69**, 45107.
- 126 R. P. Hermann, W. Scheweika, O. Leupold, R. R ffer, G. S. Nolas, F. Grandjean and G. J. Long, *Phys. Rev. B*, 2005, **72**, 174301.
- 127 M. A. Avila, K. Suekuni, K. Umeo, H. Fukuoka, S. Yamanka and T. Takabatake, *Phys. Rev. B*, 2006, **74**, 125109.
- 128 G. S. Nolas, M. Beekman, J. Gryko, G. A. Lamberton, Jr., T. M. Tritt and P. F. McMillan, *Appl. Phys. Lett.*, 2003, **82**, 910.
- 129 P. M linon, P. K gh lian, A. Perez, B. Champagnon, Y. Guyot, L. Saviot, E. Reny, C. Cros, M. Pouchard and A. J. Dianoux, *Phys. Rev. B*, 1999, **59**, 10099.
- 130 J. D. Dunitz, V. Schomaker and K. N. Trudblood, *J. Phys. Chem.*, 1988, **92**, 856.
- 131 B. C. Sales, B. C. Chakoumakos, D. Mandrus and J. W. Sharp, *J. Solid State Chem.*, 1999, **146**, 528.
- 132 B. C. Sales, D. G. Mandrus and B. C. Chakoumakos, in *Semiconductors and Semimetals*, ed. T. M. Tritt, Academic Press, San Diego, 2000, vol. 70, p. 1.
- 133 R. P. Hermann, F. Grandjean and G. J. Long, *Am. J. Phys.*, 2005, **73**, 110.
- 134 J. S. Tse and M. A. White, *J. Phys. Chem.*, 1988, **92**, 5006.
- 135 M. Beekman, G. S. Nolas, J. Gryko, G. A. Lamberton, Jr., T. M. Tritt and C. A. Kendziora, *Electrochem. Soc., Proc.*, 2004, **2003-27**, 271.
- 136 G. A. Slack, in *Solid State Physics*, ed. H. Ehrenreich, F. Seitz and D. Turnbull, Academic Press, New York, 1976, vol. 34, pp. 1–71.
- 137 X. Tang, J. Dong, P. Hitchins, O. Shebanova, J. Gryko, P. Barnes, J. K. Cockcroft, M. Vickers and P. F. McMillan, *Phys. Rev. B*, 2006, **74**, 14109.
- 138 T. C. Ozawa and S. J. Kang, *J. Appl. Crystallogr.*, 2004, **37**, 679.