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Siting of Antimony Dopants and Gallium in $Ba_8Ga_{16}Ge_{30}$ Clathrates Grown from Gallium Flux

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A series of antimony-doped $Ba_8Ga_{16}Ge_{30}$ clathrates was grown as large crystals from gallium flux. These compounds form in the cubic space group $Pm\bar{3}n$, with the unit cell parameter varying from 10.784(5) to 10.9008(6) Å as the amount of GaSb substituting for germanium atoms in the framework is increased. It was found that more antimony than extra gallium was incorporated into the material and that a specific site (the 24k Wyckoff site) was favored by this element. ^{71}Ga NMR was carried out to determine the siting of gallium; it fills the 6c site preferentially.

Introduction

In the 1960s, Hagenmuller et al. discovered group 14 analogues of the ice clathrates $Ar_8[H_2O]_{46}$ ("type 1" clathrate structure) and $(CCl_4)_8(H_2S)_{16}[H_2O]_{136}$ ("type 2" clathrate) while studying the thermal degradation process of Zintl phases such as NaSi and KGe. These clathrate compounds consist of a tetrahedrally bound framework composed of tetrel atoms (group 14 elements such as silicon or germanium) which encapsulates alkali metal guests, resulting in materials such as K_8Ge_{46} and Na_xSi_{136}.[1] Several recent investigations into the type 1 clathrate compounds indicate that the 46-atom framework of this structure (shown in Figure 1) is highly amenable to substitution. A wide range of "Zintl phase" stoichiometries has been synthesized, with specific amounts of group 12 or 13 elements incorporated into the framework to accept the charge donated from the alkali metal or alkaline earth guests. This charge balancing is exemplified by materials such as $Rb_8Al_8Si_{38}$, $Ba_8Ga_{16}Ge_{30}$, and $Cs_8Zn_4Sn_{42}$.[2,3]

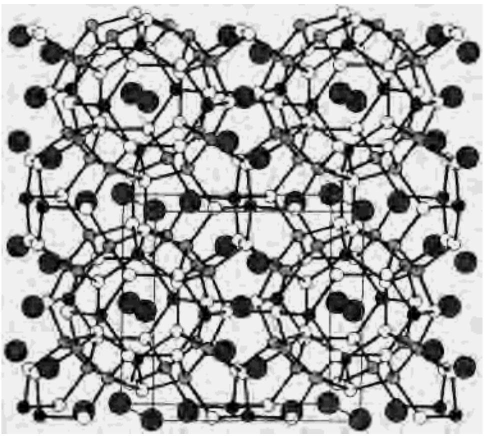

Figure 1. Structure of the type 1 clathrate. In the framework, the 6c sites are indicated by black atoms, the 16i sites by gray atoms, and the 24k sites by white atoms.

A number of clathrates have exhibited potentially useful electronic properties. Because of their complex unit cells and rattling guest atoms, these compounds have inherently low thermal conductivity. Their electrical conductivity, on the other hand, takes place predominantly through the sp^3-hybridized framework and should therefore not be hindered by the rattling of the guest species. This combination of characteristics is necessary to achieve the "phonon glass, electron crystal" balance needed for optimum thermoelectric behavior.[4] Hagenmuller's initial investigations did indicate promising thermoelectric properties in Na_xSi_{136} type 2 clathrates; recent studies on type 1 compound $Sr_8Ga_{16}Ge_{30}$ have also shown potential.[5]

Theoretical calculations on a number of $M_8Tr_{16}Tt_{30}$ clathrates (M = Ba, Sr; Tr = Ga, Al, In; Tt = Si, Ge) indicate

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Table 1. $Ba_8Ga_{16}Ge_{30}$ Clathrates Doped with Varying Amounts of Antimony

cmpd	reactant molar ratio Ba/Ga/GaSb/Ge	product stoichiometry	unit cell (Å)
BGG	8/100/0/30	$Ba_{8.00}Ga_{15.70}Ge_{29.85}Sb_{0.00}$	10.784(5)
BGG-05	8/100/0.05/29.9	$Ba_{8.00}Ga_{15.79}Ge_{29.46}Sb_{0.017}$	10.785(3)
BGG-15	8/100/0.15/29.7	$Ba_{8.00}Ga_{15.83}Ge_{29.40}Sb_{0.066}$	10.784(3)
BGG-27	8/100/0.27/29.46	$Ba_{8.00}Ga_{15.88}Ge_{29.35}Sb_{0.07}$	10.790(2)
BGG-60	8/100/0.60/28.8	$Ba_{8.00}Ga_{15.98}Ge_{29.23}Sb_{0.15}$	10.809(8)
BGG-81	8/100/0.81/28.38	$Ba_{8.00}Ga_{16.28}Ge_{29.23}Sb_{0.50}$	10.800(5)
BGG-18	8/100/1.80/26.4	$Ba_{8.00}Ga_{16.79}Ge_{27.88}Sb_{0.77}$	10.821(7)
BGG-2	8/100/4.00/22.0	$Ba_{8.00}Ga_{17.31}Ge_{25.90}Sb_{2.15}$	10.9008(6)

Table 2. Crystallographic Data for $Ba_{8.00}Ga_{17.31}Ge_{25.90}Sb_{2.15}$[a]

atom	site	x	y	z	occupancy	U_{eq}
Ba1	2a	0	0	0	1	0.011(5)
Ba2	6d	0	0.25	0.5	1	0.053(7)
Ge/Ga1	6c	0	0.5	0.25	1	0.014(4)
Ge/Ga2	24k	0	0.3084(3)	0.1183(2)	0.904(5)	0.011(3)
Sb2	24k	0	0.3084(3)	0.1183(2)	0.087(5)	As above
Ge/Ga3	16i	0.1848(2)	0.1848(2)	0.1848(2)	0.938(6)	0.011(4)
Sb3	16i	0.1848(2)	0.1848(2)	0.1848(2)	0.041(6)	As above

[a] Space group $Pm\bar{3}n$, $a = 10.9008 \pm 0.0006$ Å, $R = 0.0223$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

that the carrier density is dependent on the Ga/Ge ratio and the concentration of alkaline earth atoms.[6] Therefore, deviation from the ideal Zintl phase stoichiometry, due to variation of this Ga/Ge ratio, the introduction of dopants, and/or the presence of vacancies, should have a noticeable effect on the transport properties. A survey of recent results on clathrates bears this out. Nolas et al. investigated three polycrystalline $Sr_8Ga_{16}Ge_{30}$ clathrates with slightly different Ga/Ge ratios, finding significant variations in the transport properties of the three compounds.[5] Studies on the same clathrate with a different stoichiometry by Kuznetsov et al. indicated a different carrier concentration and effective mass.[7] Clearly, a method of fine-tuning the electronic properties is needed to optimize the performance of this family of materials.

In this work, a new avenue for the manipulation of the transport properties of these clathrates is introduced, and the utilization of flux growth in their synthesis is explored. Reaction in gallium flux has recently been shown to be a useful synthetic route to the growth of complex intermetallics such as $YNiSi_3$ and Sm_2NiGa_{12}.[8] It has also proven to be an excellent growth medium for $AE_8Ga_{16}Ge_{30}$ (AE = Ba and Sr) and $Ba_8Ga_{16}Si_{30}$ clathrates.[9] This study investigates the purposeful addition of group 15 elements into the clathrate framework in varying amounts to create a range of compounds such as $Ba_8Ga_{16+x}Sb_xGe_{30-2x}$. In the gallium flux synthesis technique used here, antimony is incorporated into the clathrate in greater amounts than the extra gallium, resulting in uncompensated doping. Antimony and gallium atoms are found to favor different framework sites, introducing the possibility that the location of nontetrel elements in the clathrate framework is determined by electronegativity.

Experimental Section

Synthesis. The clathrates were synthesized using a gallium flux technique in alumina crucibles contained within a sealed steel vessel under an argon atmosphere.[9] Reagents were measured out in the ratios shown in Table 1 and placed in the containers in an argon-filled drybox (Vac Atmospheres, with a dri-train purification system) to avoid oxidation of any of the reagents. The gallium was loaded into the crucibles first to facilitate dissolution of the other elements. The reagents used were dendritic barium (Strem Chemicals, 99.9%), gallium shot (Cerac, 99.99%), germanium powder (Strem Chemicals, 99.999%), and gallium antimonide (Cerac, 99.99%). The sealed vessels were placed in a furnace, heated to 1000 °C in 3 h, held at this temperature for 1−2 h, and then cooled to room temperature in 12 h.

To remove the excess gallium, the crucible containing the product was placed in a beaker with dilute HCl (1−2 M aqueous solution). This was then sonicated at 50 °C using a Branson 2210 sonication bath. The gallium is solubilized as colloidal gallium (evidenced by a silvery film floating on the solution) or oxidized to a soluble gallium species, and decanted from the beaker. The clathrate product remains at the bottom of the beaker as a metallic-looking solid in the form of large faceted crystals and granular powder. The sonication process is repeated with fresh aliquots of dilute acid until the liquid above the clathrate remains clear; the product is then rinsed several times with water and acetone.

Elemental and Structural Analysis. A Cameca SX50 electron probe microanalyzer was used to determine the stoichiometry of the products. A number of crystals of each product were placed within delrin rings of ∼1 in. diameter; epoxy was poured into the rings and allowed to harden. These disks were then polished to provide a flat surface of the crystals for the microprobe analysis. The disks were coated with carbon and placed in the microanalyzer. Several spots on each crystal were analyzed for Ba, Ga, Sb, and Ge using a beam current of 15 nA and a beam size of 2 mm. Only microprobe data that gave a 98−101% total mass reading were included as relevant. The resulting stoichiometries are listed in Table 1.

The most highly Sb-doped sample was used for single-crystal X-ray diffraction to facilitate the location of the antimony framework site. A small crystal (100−200 μm on a side) was mounted on a glass fiber, and room-temperature data were collected on a Siemens SMART CCD diffractometer. The SHELXTL software system was used to analyze the data and determine the structure; absorption correction was carried out using the SADABS program.[10] Results of the refinement are shown in Table 2. The unit cell parameters of all the doped clathrates (listed in Table 1) were determined by powder diffraction using a Scintag PADX diffractometer, scanning from 5° to 70° 2θ at 1° per min. Silicon was used as an internal standard.

NMR. To locate the preferential sites of the gallium in the structure, ^{71}Ga magic angle spinning (MAS) NMR was carried out on undoped $Ba_8Ga_{16}Ge_{30}$. A Bruker AMX500 MHz spectrometer

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equipped with a fast digitizer was used with a Doty high-speed MAS probe. To prevent difficulties in spinning because of the conducting nature of the material, the clathrate sample was ground up with NaCl (in a 1:1 ratio) and then placed into a 4 mm silicon nitride rotor. A one-pulse experiment was carried out with the sample spinning at 10 kHz. A 3 μs pulse was used at a resonance frequency of 153.135 MHz. The 90° pulse for this sample was found to be 9 μs; however, because of the wide resonance peaks (vide infra), the shorter pulse was used to maximize the pulse width. A total of 50000 scans were collected with a 1 μs dwell time and a 1 s relaxation delay. The Bruker XwinNMR software was used to fit the resulting spectrum. A similar experiment was carried out on strontium analogue $Sr_8Ga_{16}Ge_{30}$.

Results and Discussion

The products were isolated as a mixture of silvery, faceted, metallic looking spheroid crystals and powder, with crystal sizes ranging up to 2−3 mm in diameter. Powder X-ray diffraction did not show any significant amounts of secondary products, although in some cases a very small amount of germanium was present. Using the most highly doped material as an example, microprobe elemental analysis indicated the material consisted of the following molar percentages: 14.91% Ba, 47.97% Ge, 32.05% Ga, and 3.98% Sb. Comparison of the resulting stoichiometry of $Ba_{8.00}Ga_{17.31}Sb_{2.15}Ge_{25.90}$ to the idealized baseline compound $Ba_8Ga_{16}Ge_{30}$ indicates that four of the germanium atoms in each formula unit have been replaced by gallium and antimony atoms. Attempts to incorporate higher amounts of antimony into the clathrate were not successful, indicating an upper limit to the tractability of the framework.

The high solubility of the reactants in gallium flux allows for the formation of a uniform liquid at relatively low temperatures; the facilitated diffusion of the reactants also promotes the growth of large crystals. Because the reactants are completely dissolved, the use of a 1:1 GaSb reactant is not crucial, and use of elemental antimony would result in similar products. Attempts to make Sb-doped $Ba_8Ga_{16}Ge_{30}$ clathrates without Ga flux, using a stoichiometric mixture of the elements, does result in the formation of a clathrate phase. However, this is in the form of a powder and mixed with byproducts such as GaSb which are not present in the gallium flux products. Regardless of the use of the 1:1 GaSb reactant and the excess of gallium, the framework takes up more antimony than extra gallium; this should result in uncompensated doping of the baseline clathrate. This was a common feature of all the antimony-doped compounds, as seen in Table 1.

It should be noted that growth of undoped samples from gallium flux results in a nonideal Ga/Ge ratio. Instead of a stoichiometry of $Ba_8Ga_{16}Ge_{30}$, the compound grown from molten gallium has a stoichiometry of $Ba_{8.00}Ga_{15.70}Ge_{29.85}$. Therefore, this compound is also doped. It is understandable that synthesis in gallium flux would result in a shift away from the charge-balanced elemental ratio, although the fact that the products are apparently gallium-poor is unexpected. Separation of the electronic effects of the inadvertent doping due to the gallium flux from the effects of the added antimony is not possible at this time. Because of this, the electronic studies that were carried out on these samples are mentioned only briefly. The results of preliminary conductivity studies indicate that the flux-grown undoped and antimony-doped samples exhibit semiconducting behavior (in terms of temperature dependence of the resistivity) up to a certain doping level, at which metallic behavior ensues.[11] The measured single-crystal conductivities are all in the 100−600 S/cm range, which is lower than the values reported for ingots and single crystals of the undoped $Ba_8Ga_{16}Ge_{30}$ grown by traditional high-temperature annealling methods (1400−1500 S/cm).[5,7]

The lower conductivity is likely due to scattering from the dopant atoms and other defects (such as vacancies) introduced by the comparatively fast reaction times used in this gallium flux synthesis technique. Instead of the thermodynamically favored materials resulting from standard high temperature reaction methods, rapid flux growth can result in kinetically controlled products. Recent work on intermetallics grown from aluminum flux indicates that this technique may permit the formation of more disordered structures than those produced by arc melting and annealling. A comparatively fast growth of $Gd_{1.33}Pt_3Al_8$ from Al flux produces a disordered, crystallographically averaged substructure of the $Gd_4Pt_9Al_{24}$ structure type that results from lengthy annealling.[12] Also, a novel $A_3Na_{10}Sn_{23}$ pseudoclathrate was recently obtained from tin flux, a structure composed of slabs of fused pentagonal dodecahedra cages alternating with disordered layers of isolated tin tetrahedra and cations.[13] Grown from an excess of tin at low temperature (400 °C), this compound could be considered an intermediate in the oxidative condensation of Sn_4^{4-} tetrahedra into the clathrate type 2 framework. Topotactical oxidative condensation of Si_4^{4-} units is a likely mechanism for the solid-state conversion of the NaSi Zintl phase to the Na_xSi_{136} and Na_8Si_{46} clathrates; a similar process may occur within a tin or gallium flux.[1,11] Because the fast crystal growth of $Ba_8Ga_{16}Ge_{30}$ from gallium flux is likely to result in disorder and/or defects, the siting of elements and amount of vacancies in this compound is of interest. Zone refining experiments are currently underway to further explore the effects of vacancies and to compare the properties of flux-grown clathrates to annealled clathrates.[14]

In the refinement of the single-crystal X-ray data of $Ba_{8.00}Ga_{17.31}Sb_{2.15}Ge_{25.90}$, initially reported in ref 15, the structure was assigned to the cubic space group $Pm\bar{3}n$ with a unit cell edge of 10.9008 ± 0.0006 Å. The antimony dopant was initially assigned to the 6c site, but the thermal parameters were very high compared to the other two framework sites. For such a small amount of antimony, all the framework sites should have similar thermal parameters because they are mostly Ge or Ga atoms in similar coordination environ-

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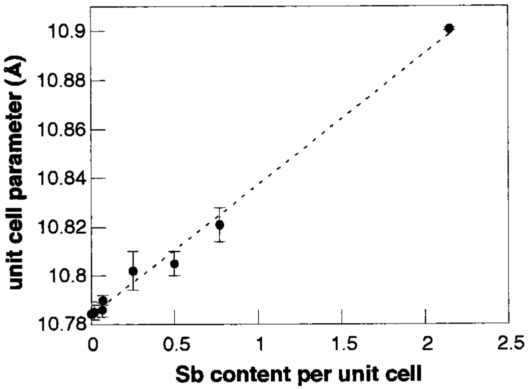

Figure 2. Plot of unit cell edge vs antimony content for the antimony-doped $Ba_8Ga_{16}Ge_{30}$ clathrates. The linear dependence indicates agreement with Vegard's law.

ments. A number of trials were attempted in which the thermal parameters were made similar, and it was found that the Sb occupancy in the 6c site dropped to zero and the Sb occupancy in the 16i and 24k sites rose. The final result, with an R value of 0.0233 ($R = \sum||F_o| - |F_c||/|F_o|$; for $I > 2\sigma$), had similar thermal parameters in all three framework sites (as expected), with antimony preferentially in the 24k site. A small number of vacancies are also indicated by the crystal structure refinement, in agreement with elemental analysis which indicates 45.4 framework atoms per unit cell.

Further verification of the substitution of framework germanium by GaSb is implied by the expansion of the unit cell in comparison to the baseline compound $Ba_8Ga_{16}Ge_{30}$. Replacement of germanium atoms by gallium and the much larger antimony results in an increase of the unit cell edge from 10.7844 Å for the "undoped" compound to 10.9008 Å for the highly doped material. This effect is observed in all the antimony-doped compounds synthesized in this work. The antimony molar concentration is plotted against the unit cells of the clathrates in Figure 2; it is seen that Vegard's law (that the lattice constant should change linearly with changing content) is obeyed.

It was not possible to distinguish between Ga and Ge in the refinement of the X-ray data because of their similar electron density. Analysis of bond lengths in the clathrate structure may aid in the determination of preferential framework siting of atoms. A survey of known compounds indicates that Ge−Ge bonds in Zintl and intermetallic phases commonly range between 2.4 and 2.5 Å; Ga−Ga bonds are usually longer, between 2.5 and 2.7 Å on average.[16] The longest framework bonds in $Ba_{8.00}Ga_{17.31}Sb_{2.15}Ge_{25.90}$ are found between the 6c site and the four 24k sites bonded to it at a distance of 2.534(4) Å, and between linked 24k sites (2.578(3) Å). The shortest bonds, at 2.462(3) Å, are between 16i sites. This could indicate that the 16i sites are preferentially filled by germanium, with the gallium and antimony atoms distributed among the 6c and 24k sites. However, bond lengths are also impacted by the relative energies of the atomic orbitals on the framework atoms, which are affected by other structural factors such as bond angles, so the small variation in bond lengths is likely not definitive evidence of preferential siting.

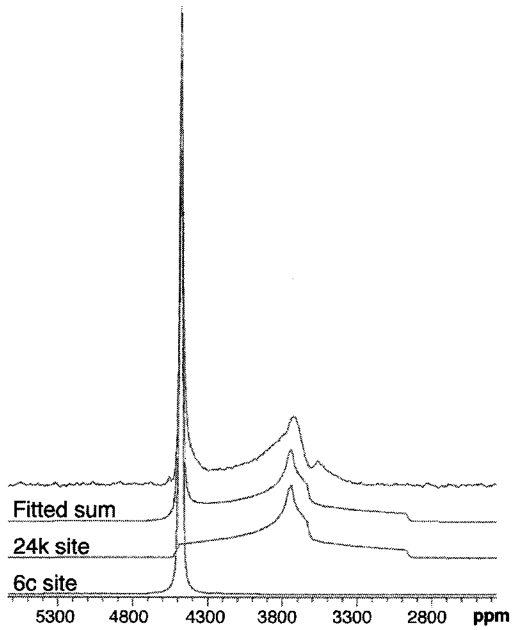

Figure 3. ^{71}Ga MAS NMR of undoped $Ba_8Ga_{16}Ge_{30}$. The top curve is the experimental data, the second is the fit, and the third and fourth are the individual resonance fittings for the 24k site and the 6c site, respectively.

To further investigate gallium siting in the clathrate framework, ^{71}Ga NMR was carried out on $Ba_8Ga_{16}Ge_{30}$. The resulting spectrum is shown in Figure 3. A similar NMR study was carried out on $Sr_8Ga_{16}Ge_{30}$; the data for the strontium analogue are identical. Two of the three possible framework sites are represented in the spectrum, one with a symmetric narrow peak, and one with a very large quadrupolar pattern. Both signals are Knight shifted into the region of metallic gallium (4000 ppm),[17] indicating that gallium in the framework is interacting with conduction electrons. The fact that $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Ge_{30}$ have identical ^{71}Ga NMR spectra suggests that the gallium atoms in both frameworks have very similar electronic environments. This is also indicated by Ga K-edge XANES data for the two clathrates; the absorption edge has approximately the same value for the two clathrates and is close to that of metallic gallium.[9]

From the site symmetries depicted in Figure 4, it is clear that the 6c site is highly symmetric; a gallium atom on this site would experience no electric field gradient and therefore would exhibit no quadrupolar broadening. The narrow symmetric peak at 4478 ppm likely corresponds to gallium on this site. The remaining signal can be fit to a quadrupolar resonance at 4509 ppm, with a quadrupolar coupling constant (QCC) of 22.26 MHz and an asymmetry parameter (η) of 1.0. This indicates a gallium site with a very large and asymmetric (nonaxial) electric field gradient. Looking at the local environments of the three framework sites, it is apparent

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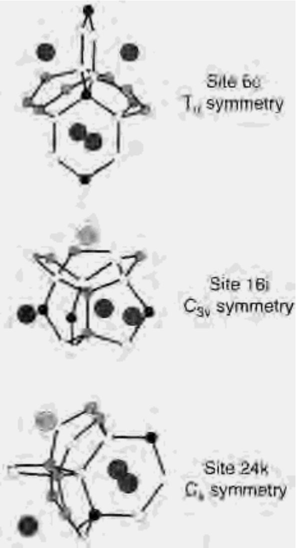

Figure 4. Local site symmetries of the three framework sites in $Ba_8Ga_{16}Ge_{30}$. The 6c sites are indicated by black atoms, 16i sites by gray atoms, and 24k sites by white atoms. The larger light spheres correspond to barium in a 2a site; the large dark spheres correspond to barium in 6d sites.

that the 24k site has a low nonaxial symmetry. The cage guests are distributed irregularly about this site (two Ba 6d sites at a distance of 3.623 Å, one 2a Ba site at 3.554 Å, and one 6d site at 4.159 Å). Also, because this position constitutes part of the hexagonal faces of the tetrakaidecahedral cages in the structure, the framework angles at this site are very distorted from the 109.5° expected for tetrahedral coordination. The 6-ring in the clathrate I structure is highly irregular, with two angles of 110.9° (the vertices of which are the 6c site), and four angles of 124.5° (the vertices of which are 24k sites). The 24k site is therefore the likely source of the second NMR signal.

The integrated ratio of these two signals in the NMR spectrum is 1:2.19 (6c:24k). If these resonances represent the total amount of gallium in the sample, this would indicate that there are 5 gallium atoms in the six framework 6c sites and 11 gallium atoms in the 24k sites. Therefore, the group 13 element preferentially fills the 6c site in these compounds. There is the possibility that some of the gallium occupies the 16i site; this signal would likely be hidden beneath the large quadrupolar pattern of the 24k site. Differentiation of these signals would be very difficult; the extremely large QCC makes techniques such as MQMAS problematic. Another complicating issue is that, while some of the 6c Ga sites are surrounded by four 24k sites occupied by Ge atoms, other 6c sites are coordinated to four 24k sites which contain a mixture of Ge atoms and the remaining Ga atoms. This may be the source of the observed line broadening and the slight asymmetry in the 6c resonance.

The NMR results discussed here are in disagreement with a recent neutron powder diffraction study on $Sr_8Ga_{16}Ge_{30}$, which indicated a fully disordered distribution of gallium on all the framework sites.[18] However, a preference of the triel elements (Al, Ga, In) for the 6c site is indicated by many structural reports in other clathrate literature. According to Eisenmann's single-crystal diffraction work on $Ba_8Ga_{16}Si_{30}$, there are 3.6 gallium atoms on the 6c site, 1.2 gallium atoms on the 16i site, and 9.8 gallium atoms on the 24k site. In $Ba_8Al_{16}Ge_{30}$, the 6c site is completely filled by aluminum, with most of the remaining aluminum going in the 16i site.[19] A preference for the 6c site has also been found for the group 12 framework elements in clathrates such as $Ba_8Cd_8Ge_{38}$ and $Ba_8Zn_8Ge_{38}$.[20] In an exploration of transition metal incorporation into the clathrate structure, Cordier and Woll found that Ni, Pd, Pt, Cu, Ag, and Au also preferentially occupied the 6c site to form clathrates such as $Ba_8Au_6Ge_{40}$.[21] In addition to these nontetrelide elements, defects are also located at this site; in Corbett's crystallographic analysis of K_8Sn_{44}, the two vacancies per unit cell were found at the 6c position.[22]

The observed siting of gallium in the 6c and 24k sites is also in agreement with density functional calculations that were recently carried out to determine which arrangement of elements in the framework has the lowest energy.[6] The most stable configurations were those with gallium atoms occupying sites in the 6-rings but distributed in a manner that avoids Ga−Ga bonds. Additional support for preferential siting of gallium in the 6c site is found in the examination of framework electron density in $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Ge_{30}$ using the maximum entropy method on single-crystal X-ray data.[9] Relative to reference models having random distributions of neutral Ga and Ge atoms in the framework, the 6c sites were found to be depleted of electrons, indicating a greater presence of gallium compared to germanium.

Are the 6c sites therefore the preferred location for all nontetrelide elements in the clathrate framework? This idea would seem to contradict the results shown in this work, which place antimony preferentially in the 24k and 16i sites. Literature discussing group 15 elements in the clathrate framework is scarce, as the introduction of these moieties into clathrate synthesis has not yet been extensively explored. According to the structures of halogen-containing "inverse clathrates" such as $Ge_{38}P_8I_8$, it appears that the group 15 elements in these compounds prefer the 16i framework sites. Eight Ge atoms and eight pnictogen atoms are actually ordered in the 16i sites, resulting in a symmetry lowering from $Pm\bar{3}n$ to $P\bar{4}3n$.[23] However, because the halogen guests in the cages are very different from the alkali metal and alkaline earth atoms in the normal clathrates, a comparison between these systems might not be appropriate. Because the antimony-doped clathrates studied here contain barium guests, they serve as a more optimal analogous system. Also appropriate for comparison are phosphorus doped $Ba_8Ga_{16}Ge_{30}$ compounds. Initial single-crystal X-ray data on a compound with stoichiometry $Ba_8Ga_{18.11}P_{2.19}Ge_{24.34}$ ($a = 10.7708 \pm 0.0007$ Å, the smaller unit cell another indication

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of replacement of Ge by P atoms), synthesized and analyzed in a similar manner as the antimony doped compounds studied here, indicate that phosphorus preferentially occupies the 16i site.[11]

These results seem to suggest that nontetrel elements distribute themselves in the clathrate framework according to electronegativity. Electropositive elements (Ga, Al, Zn, Cd, transition metals) occupy the 6c framework site preferentially; electronegative elements such as antimony and phosphorus, on the other hand, are found in 24k or 16i sites. Similar site segregation of elements according to electronegativity was observed by Lee and Miller in the ternary R-phase $Mg_{32}(Zn,Al)_{49}$ and a lithium-containing quaternary variant of this structure. Relative Mulliken population studies confirmed that sites in the structure are positively or negatively polarized relative to each other, and the site potentials are in agreement with the predominance of electropositive (Mg, Li) or electronegative elements (Al, Zn) found on each site.[24] It is not unreasonable to assume a similar mechanism is at work in the clathrate structure.

Conclusion

The possibility that electronegativity is a controlling factor in the placement of elements in the clathrate framework is important to many aspects of clathrate research. Framework modification through doping or substitution is an obvious avenue to explore in the optimization of the electronic properties of these materials. The ability to predict which sites the substituting elements will occupy will aid in determining which of the possible doping scenarios is most likely to lead to the desired properties.

Synthesis in gallium flux has proven to be a useful method for growing large crystals of clathrates which also allows for the incorporation of dopants. The individual effects of these two new variables, new synthesis technique and antimony dopant, must be separated, however. Experiments are currently underway to isolate the effect of the gallium flux synthesis on the Ga/Ge ratio and amount of vacancies in $Ba_8Ga_{16}Ge_{30}$. Further investigations into flux growth of $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Si_{30}$ are also in progress. These systems have their own idiosyncracies to be explored, such as the fact that their frameworks do not appear to incorporate dopants to the extent seen for $Ba_8Ga_{16}Ge_{30}$.

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