

# Gallium Antimonide-Doped Germanium Clathrate— A *p*-Type Thermoelectric Cage Structure

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Received October 5, 1999; in revised form December 27, 1999; accepted January 10, 2000

A germanium clathrate compound doped with gallium antimonide has been synthesized and characterized. The structure of  $\text{Ba}_8\text{Ga}_{16}(\text{GaSb})_x\text{Ge}_{30-2x}$  with  $x = 2$  was determined using single-crystal X-ray analysis, and the Sb atoms were found to be selectively sited. A slight excess of antimony was confirmed by microprobe elemental analysis, resulting in uncompensated doping of the framework. A positive and relatively high Seebeck coefficient of  $100 \mu\text{V/K}$  indicates this compound is a potential *p*-type thermoelectric material. Single-crystal temperature-dependent conductivity indicates that the sample behaves as a poor metal. This is the first example of *p*-doping reported for clathrates. © 2000 Academic Press

**Key Words:** *p*-type thermoelectric; germanium clathrate; selective siting of dopant.

## INTRODUCTION

Germanium clathrate compounds have inspired much interest recently because of their potential use as thermoelectric materials (1–3). The large unit cell and cage structure of these materials lead to an inherently low thermal conductivity  $\kappa$ , and the adjustment of the transport properties by modification of the guests in the cage and the composition of the framework allows for optimization of the electrical conductivity  $\sigma$  and Seebeck coefficient  $S$ . All of these factors are being explored to create a material with a high thermoelectric figure of merit  $ZT = S^2\sigma T/k$ . Of the two main clathrate structures, exemplified by the archetypes  $\text{Na}_8\text{Si}_{46}$  and  $\text{Na}_x\text{Si}_{136}$  ( $3 < x < 24$ ), it is the former “clathrate I” type that has been predominantly investigated of late (Fig. 1). In addition to the thermoelectric properties and superconductivity found for some materials with this structure, this type I configuration also allows for a large amount of framework substitution (4, 5). A number of the silicon or germanium atoms can be replaced by group 12 or 13 species. A charge-balanced zintl-phase model has been derived for this family of compounds, with the alkali metal or alkaline earth guest donating its charge to the framework, resulting in stoichiometries such as  $\text{K}_8\text{Al}_8\text{Ge}_{38}$  and

$\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  in which the group 13 metal acts as an electron-accepting site (6,7). In the apparently charge-unbalanced structures such as  $\text{K}_8\text{Sn}_{46}$ , vacancies have been found on specific framework sites, leading to an actual stoichiometry of  $\text{K}_8\text{Sn}_{44}[\ ]_2$ , where the three-bonded tin atoms act as electron-accepting sites (8). Despite this evidence, the hypothesis of full charge transfer from guest atom to host framework to form a closed-shell zintl phase has been called into question by recent experiments which indicate that the guest is close to neutral in some cases (2,9).

In this work, we were able to substitute GaSb for some of the germanium atoms in the framework of  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ . It was found that more antimony than extra gallium was incorporated into the framework (inconsistent with the charge-balanced zintl-phase model), and that a specific site was favored by this element. This excess antimony results in *p*-type conductivity and a positive Seebeck coefficient of  $100 \mu\text{V/K}$ . The temperature-dependent conductivity measurements confirm that it is a poor metal, with resistance rising with temperature. This compound is the first *p*-type clathrate reported.

## EXPERIMENTAL PROCEDURE

The clathrate was synthesized in an alumina crucible contained within a sealed steel vessel under an argon atmosphere. Reagents were measured out and placed in the container in an argon-filled drybox (Vac Atmospheres, with a dri-train purification system) to avoid oxidation of any of the reagents. 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%). A specialized technique was used to grow crystals of the product which will be described in a future patent and publication (10).

A Cameca SX50 electron probe microanalyzer was used to determine the stoichiometry of the product. A number of crystals were placed on a sticky substrate, using an optical microscope to attempt to orient a flat plane parallel to the substrate surface (and therefore perpendicular to the

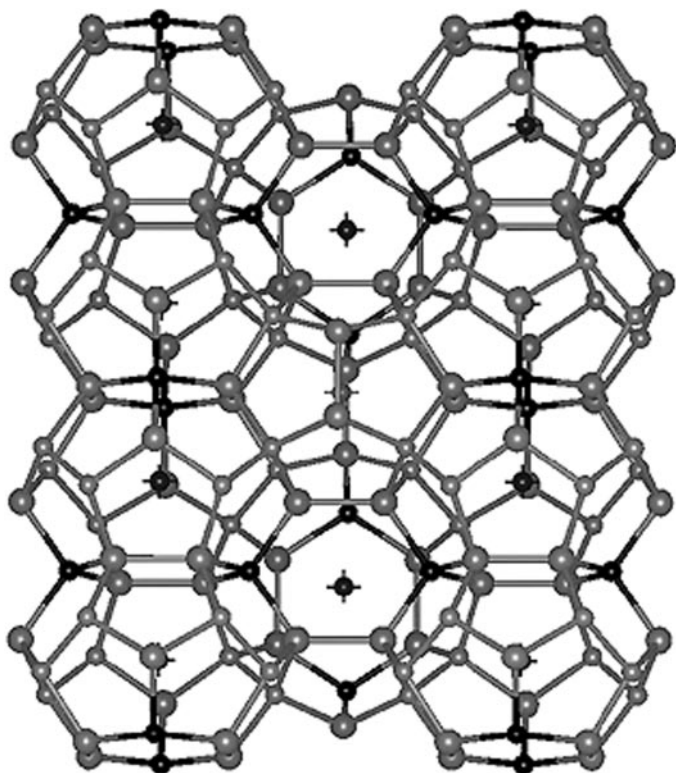


FIG. 1. Clathrate type I structure. In the framework, the 6*c* sites are indicated by the black atoms, the 16*i* sites by the small gray atoms, and the 24*k* sites by the large gray atoms.

electron beam of the microanalyzer). The samples were then coated with carbon and placed in the microanalyzer. Several spots on any apparent faces normal to the beam (judged by the brightness of the scattering and the size of the region in focus) were analyzed for Ba, Ga, Sb, and Ge. Only spots that gave a 98–101% total mass reading were included as relevant. A beam current of 15 nA and a beam size of 2  $\mu\text{m}$  was used to collect all data.

For single-crystal X-ray diffraction, a small crystal (100–200  $\mu\text{m}$  on a side) was mounted on a glass fiber and room temperature data were collected on a Siemens SMART CCD diffractometer. The SHELXTX software system was used to analyze the data and determine the struc-

ture. An initial tetragonal supercell was indicated, but the cubic Niggli cell was recommended and used. Results of the refinement are shown in Table 1.

Seebeck measurements were carried out on pressed pellets at several different temperatures on a home-built apparatus based on the design described in Ref. (11). The sample was held between copper blocks heated to different temperatures using nichrome wire. Copper leads were used to read the voltage difference across the sample; the temperatures of the blocks were read with type K thermocouples embedded in the copper blocks so that the tips were very close to the faces of the sample. Single crystals for conductivity measurements were prepared by embedding a large crystal in soluble thermoset and sanding it down to a rectangular shape. After removal of the thermoset, leads were soldered onto the crystal in a van der Pauw geometry, and measurements were taken in a small temperature range.

## RESULTS AND DISCUSSION

The product was isolated as a mixture of gray, faceted, metallic-looking crystals and powder, with crystal sizes ranging up to 2–3 mm on a side. Powder diffraction (Scintag PADX diffractometer) did not show any unreacted starting materials or secondary products. 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  $\text{Ba}_{8.05}\text{Ga}_{17.31}\text{Sb}_{2.15}\text{Ge}_{25.90}$  to the undoped “baseline” compound  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  indicates that four of the germanium atoms in each formula unit have been replaced by gallium and antimony atoms, with the amount of antimony higher than the amount of gallium. Despite the fact that the gallium antimonide is introduced into the synthesis mixture as the 1:1 compound, more antimony is taken up by the framework than extra gallium; this should result in uncompensated doping of the baseline clathrate.

In the refinement of the single-crystal X-ray data, the structure was assigned to cubic space group  $Pm\bar{3}n$  with a unit cell edge of  $10.9008 \pm 0.0006 \text{ \AA}$ . It was not possible to distinguish between Ga and Ge in the refinement. The “rattling” of the barium atoms in the larger cages of the

TABLE 1  
Refinement Results

Atom	Site	x	y	z	Occupancy	Thermal parameters
Ba1	2 <i>a</i>	0	0	0	1	0.01081, 0.01081, 0.01081, 0, 0, 0
Ba2	6 <i>d</i>	0	0.25	0.5	1	0.07002, 0.01864, 0.07002, 0, 0, 0
Ge1, Ga1	6 <i>c</i>	0	0.5	0.25	1	0.01239, 0.01239, 0.01654, 0, 0, 0
Ge2, Ga2	24 <i>k</i>	0	0.308405	0.118288	0.90492	0.01109, 0.01049, 0.01240, – 0.00130, 0, 0
Sb2	24 <i>k</i>	0	0.308405	0.118288	0.08780	As above
Ge3, Ga3	16 <i>i</i>	0.184802	0.184802	0.184802	0.93840	0.01090, 0.01090, 0.01090, – 0.00106, – 0.00106, – 0.00106
Sb3	16 <i>i</i>	0.184802	0.184802	0.184802	0.04191	As above

clathrate (the  $6d$  site)—which aids in lowering the thermal conductivity of the material—is evidenced by large anisotropic thermal parameters (1,3). The antimony dopant was initially assigned to the  $6c$  site which resulted in an  $R$  value of 2.36, but the thermal parameters were very high compared to those of 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 in similar coordination environments. Furthermore, the total antimony occupancy determined by the X-ray refinement was off by a factor of approximately 2 from the results of the microprobe analysis. 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 2.33, 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. These are located on the  $16i$  site, which is only 98% filled.

The total amount of antimony indicated by the final refinement of the site occupancies is in close agreement with the stoichiometry determined by elemental analysis (2.78 Sb atoms in the X-ray formula unit, vs 2.15 by microprobe). As noted above, in the initial calculation with Sb in the  $6c$  site, the resulting total occupancy indicated far more antimony present in the structure than was available in the synthesis mixture, another sign that the initial refinement was wrong. 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  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ . Replacement of four germanium atoms by gallium and the much larger antimony results in an increase of the unit cell edge from 10.7668 Å for the “undoped” compound (7) to 10.9008 Å for the doped material.

The observed siting of the antimony in  $\text{Ba}_{8.05}\text{Ga}_{17.31}\text{Sb}_{2.15}\text{Ge}_{25.90}$  is in contrast to the previously observed preference of defects and nongermanium elements in a survey of published alkaline earth-containing clathrate structures. In most compounds such as  $\text{Ba}_8\text{Ga}_{16}\text{Si}_{30}$  and  $\text{K}_8\text{Al}_8\text{Ge}_{38}$ , the group 13 elements are found predominantly in the  $6c$  site (6, 12). However, in Menke and von Schnering’s work on inverse clathrates (including single-crystal data on  $\text{Ge}_{38}\text{P}_8\text{Br}_8$  and  $\text{Ge}_{38}\text{P}_8\text{I}_8$ ), they found the group 15 elements preferred to occupy the  $8e$  sites in the  $P4-3n$  structures, equivalent to the  $16i$  sites in the  $Pm-3n$  space group (13). This is in agreement with our findings, and could indicate an organization of framework sites by electronegativity, with the more electropositive group 13 elements preferring the  $6c$  sites, and the more electron-rich group 15 elements occupying the  $16i$  and  $24k$  sites.

The Seebeck coefficient was found to be  $100 \mu\text{V}/\text{K}$  at  $40^\circ\text{C}$ , rising slightly with temperature. The conductivity

drops with temperature, going from 224 S/cm at 273 K to 88 S/cm at 323 K. The positive Seebeck value indicates that this clathrate has  $p$ -type conductivity, and the temperature dependence and magnitude of the conduction suggest that it is a poor metal. Both characteristics are somewhat surprising. A charge-balanced zintl-phase clathrate such as  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  should be a semiconductor, with the electrons from the alkaline earth guest filling the vacancies in the valence bands of the electron-deficient gallium–germanium framework. Doping this compound with antimony would be expected to lead to  $n$ -type semiconducting behavior. The results observed here (and on the study of the baseline compound, which has a conductivity in the 400 S/cm range that increases as the temperature is lowered (4)) indicate that charge transfer between guest and framework is not complete. Therefore it is the unfilled framework valence band that controls electronic transport; introducing defects or dopants into the clathrate framework consequently has a great effect on the electronic properties of the material. It is possible that the addition of antimony results in the filling of this valence band, and conduction through higher energy bands with more barium character. Transport through such bands would be hindered by the phonons associated with the rattling of the barium atoms, resulting in poor conductivity. Detailed theoretical calculations are in progress to determine how the defect structure affects the thermoelectric behavior. A compound has been prepared with less antimony dopant ( $\text{Ba}_8\text{Ga}_{16}(\text{GaSb})_x\text{Ge}_{30-2x}$  with  $x = 0.81$ ); initial studies indicate it is also  $p$ -type and has a room temperature conductivity of 280 S/cm, in between that of the baseline clathrate and the heavily doped material studied here. Further synthesis of clathrates with various antimony doping levels, Hall effect measurements, and band structure calculations are being carried out to explain these observations and optimize the thermoelectric properties of these materials.

## CONCLUSIONS

In the process of replacing framework germanium of the clathrate  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  with gallium antimonide, excess antimony was incorporated into the material, resulting in a stoichiometry of  $\text{Ba}_{8.05}\text{Ga}_{17.31}\text{Sb}_{2.15}\text{Ge}_{25.90}$ . The antimony exhibits preferred siting on the  $24k$  crystallographic sites. Conductivity characteristic of a  $p$ -type poor metal results from this doping. This is the first  $p$ -type clathrate reported, and is further evidence of the important role of defects and dopants in controlling the transport properties of these clathrates. Work is in progress to optimize the thermoelectric behavior of these materials.

## ACKNOWLEDGMENTS

The authors thank Dan Bryan and Vojislav Srdanov for helpful discussions about this work. This research was supported by ONR Grants numbers N00014-96-1-0053 and N00014-99-1-0266.

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