

III–V Clathrate Semiconductors with Outstanding Hole Mobility: $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ and $\text{A}_8\text{Ga}_{27}\text{Sb}_{19}$ ($\text{A} = \text{Cs}, \text{Rb}$)Bryan Owens-Baird,[#] Jian Wang,[#] Suyin Grass Wang, Yu-Sheng Chen, Shannon Lee, Davide Donadio, and Kirill Kovnir*Cite This: *J. Am. Chem. Soc.* 2020, 142, 2031–2041

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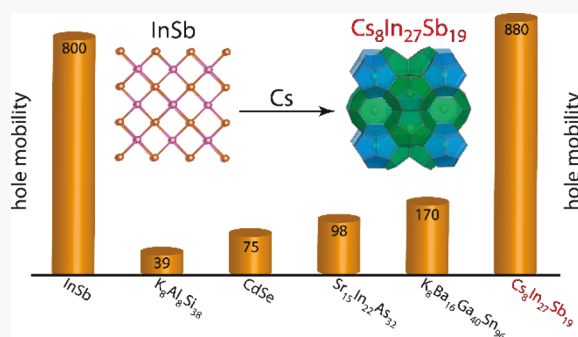


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ABSTRACT: Three novel unconventional clathrates with unprecedented III–V semiconducting frameworks have been synthesized: $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$, $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$, and $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$. These clathrates represent the first examples of tetrel-free clathrates that are completely composed of main group elements. All title compounds crystallize in an ordered superstructure of clathrate-I in the $Ia\bar{3}$ space group (No. 206; $Z = 8$). In the clathrate framework, a full ordering of {Ga or In} and Sb is observed by a combination of high-resolution synchrotron single-crystal and powder X-ray diffraction techniques. Density functional theory (DFT) calculations show that all three clathrates are energetically stable with relaxed lattice constants matching the experimental data. Due to the complexity of the crystal structure composed of heavy elements, the reported clathrates exhibit ultralow thermal conductivities of less than $1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at room temperature. All compounds are predicted and experimentally confirmed to be narrow-bandgap p-type semiconductors with high Seebeck thermopower values, up to $250 \mu\text{V}\cdot\text{K}^{-1}$ at 300 K for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$. The latter compound shows carrier concentrations and mobilities, $1.42 \times 10^{15} \text{ cm}^{-3}$ and $880 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, which are on par with the values for parent binary InSb, one of the best electronic semiconductors. The high hole carrier mobility is uncommon for complex bulk materials and a highly desirable trait, opening ways to design semiconducting materials based on tunable III–V clathrates.



INTRODUCTION

The discovery of the first transistor based on Ge revolutionized the electronics device field. Soon after the discovery, it was realized that Ge was not the only choice for semiconductors, and II–VI and III–V materials were intensively investigated in various forms from bulk single crystals down to nanocrystals.^{1–5} The III–V proved to be superior than II–VI materials due to higher covalency and substantial carriers mobilities. For example, p-type InSb has a mobility of $\sim 800 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,⁶ which is comparable to the mobilities of p-type Si ($\sim 500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^{7,8} and Ge ($\sim 2000\text{--}2300 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^{9–11} at similar carrier concentrations. Additionally, III–V materials have been shown to be highly tunable compared to pristine Si and Ge. Due to their outstanding mobilities, binary III–V semiconductors have been used in a number of commercial high-profile electronic applications, such as integrated circuits, LEDs, and high-performance photovoltaics.^{12–17}

Different allotropic modifications for Si and Ge have been reported, including empty clathrate structures, Ge_{136} and Si_{136} , in which the tetrahedrally coordinated Si or Ge form three-dimensional frameworks with empty polyhedral cages.^{18,19} Filling cages in the tetrahedral clathrate frameworks (Figure 1) with various cations, in addition to substituting Si or Ge with elements of groups 10–17, results in over 200 different

clathrate compositions. The mobility of typical Si and Ge-based clathrates is lower than that for the elemental semiconductors, for instance, $4\text{--}8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$,²⁰ $7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $\text{Ba}_8\text{Al}_{16}\text{Si}_{30}$,²¹ $21 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $\text{Ba}_8\text{Cu}_{4.61}\text{Ga}_{1.04}\text{Ge}_{40.35}$,²² $39 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $\text{K}_8\text{Al}_8\text{Si}_{38}$,²³ $50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $\text{Cs}_8\text{Ba}_{16}\text{Ga}_{40}\text{Sn}_{96}$,²⁴ and outstanding report of $170 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $\text{K}_8\text{Ba}_{16}\text{Ga}_{40}\text{Sn}_{96}$.²⁵ Clathrates are actively studied because of their thermoelectric, superconducting, and photovoltaic properties. It has been a longstanding goal to design novel clathrates composed of III–V group elements as the framework, leading to significantly higher mobilities that will boost their thermoelectric and photovoltaic potential.

Conventional clathrates, with frameworks composed of tetrel elements of group 14 (Si, Ge, or Sn), can be partially replaced with group 13 triel elements (Al, Ga, or In) to realize the electron-balanced composition, i.e., four electrons per framework atom in the clathrate to achieve tetrahedral

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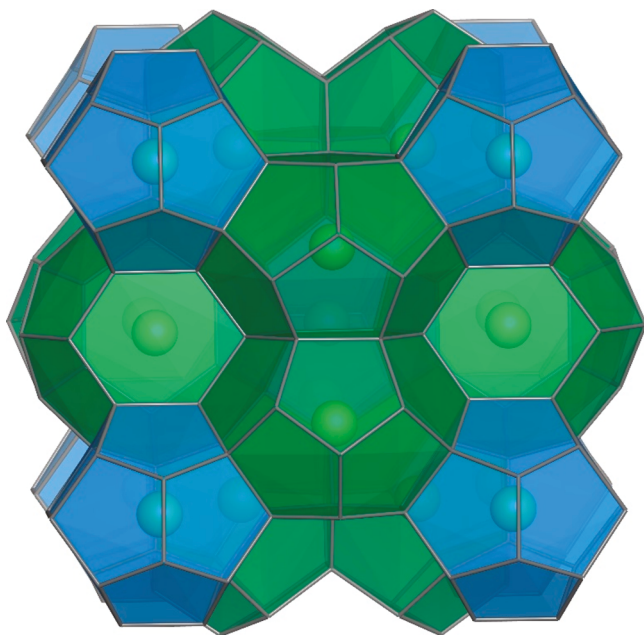


Figure 1. Crystal structure of cubic clathrate-I with two types of polyhedral cages emphasized. Pentagonal dodecahedra are shown in blue, and tetrakaidecahedra are shown in green.

coordination. For example, the excess of electrons from K, Cs, or Ba guest cations is compensated with the replacement of tetrel with triel atoms, such as $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$,²⁶ $\text{Cs}_8\text{Ga}_8\text{Si}_{38}$,²⁷ $\text{K}_8\text{In}_8\text{Sn}_{38}$,²⁸ and $\text{Ba}_8\text{Al}_{16-x}\text{Si}_{30+x}$.²⁹ Clathrate frameworks can be made tetrel-free, using transition metals and phosphorus frameworks $\{\text{Ni}, \text{Cu}, \text{Zn}, \text{Au}\}$ –P with Ba, Sr, and La as guest cations, e.g., $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$, $\text{Ba}_8\text{Au}_{16}\text{P}_{30}$, BaNi_2P_4 , or SrNi_2P_4 .^{30–38} To date, few examples of As- or Sb-containing tetrel-free clathrates have been reported: $\text{Cs}_8\text{Zn}_{18}\text{Sb}_{28}$,³⁹ $\text{Rb}_8\text{Zn}_{18}\text{As}_{28}$,⁴⁰ and $\text{Ba}_8\text{Cu}_{16}\text{As}_{30}$.⁴¹ We hypothesized that clathrate frameworks could be composed solely from triels and pnictogens, similar to replacing Ge with GaAs in simple semiconductors. To create a Si- or Ge-free clathrate, two criteria must be met: (i) an electron balance for the composition and (ii) a cation/framework size match. For example, for clathrate-I structures, with the formula $\text{A}_8(\text{In}, \text{Sb})_{46}$, where A is a monovalent alkali guest cation that donates its valence electrons to the framework, the composition $\text{A}_8\text{In}_{27}\text{Sb}_{19}$ is electron-balanced.

The total number of available valence electrons is $1 \times 8(\text{Cs}) + 3 \times 27(\text{In}) + 19 \times 5(\text{Sb}) = 184$, exactly 4 electrons per 46 framework atoms required for tetrahedral bonding. To select an alkali cation of proper size, the reported tetrel clathrates were analyzed. The triel-antimony frameworks $\text{In}_{27}\text{Sb}_{19}$ and $\text{Ga}_{27}\text{Sb}_{19}$ have average framework covalent radii of 1.41 and 1.31 Å, respectively. This greatly exceeds the average radii of Si- and Ge-based clathrates (~ 1.2 Å) but is comparable to the framework radii of Cs–Sn and Rb–Sn clathrates (~ 1.4 Å).⁴² Thus, we focused on A–{Ga, In}–Sb systems (A = Rb, Cs). In this work we report the first examples of unconventional clathrates with an entirely III–V framework. Synthesis guided by *in situ* studies, an ordered clathrate superstructure, thermal stability, calculated electronic structure, and outstanding transport properties for the novel clathrates are discussed.

RESULTS AND DISCUSSION

Crystal Structure of $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$. $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ crystallizes in the body-centered $Ia\bar{3}$ space group (No. 206; $Z = 8$) with a unit cell length of $a = 24.4620(8)$ Å at 100 K. This $2a \times 2a \times 2a$ clathrate superstructural unit cell is 8 times larger than the $Pm\bar{3}n$ archetypical type-I clathrate. In the $Ia\bar{3}$ structure the 10 framework sites are able to accommodate $27 \times 8 = 216$ In and $19 \times 8 = 152$ Sb atoms without mixed occupancy of the atomic site by elements of different chemical nature. The ordered unit cell has 13 crystallographic positions: 8a, 8b, two 16c, two 24k, and seven 48e sites (Figure 2; Tables S1–S3).

Refinement of the crystal structure of $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ is challenging because In and Sb have similar X-ray scattering factors, atomic numbers 49 and 51. Both single crystal and powder synchrotron diffraction techniques showed an existence of superstructure with respect to traditional clathrate-I primitive cubic cell (see Supporting Information for details). Synchrotron single crystal X-ray diffraction data set was collected up to high $\sin\theta/\lambda = 1.19$ and data/parameters ratio of 203, which allow for distinguishing In and Sb sites in the final refinement. After all atomic positions had been found in the initial solution, the assignment of In and Sb within the 10 framework positions followed. Initially, In and Sb were randomly assigned to the sites and the model was refined. Each site occupancy was then allowed to individually refine with the notion that for the incorrectly assigned atom type the site occupancy would rise or lower toward the correct atom type. For instance, an Sb site with site occupancy refined to

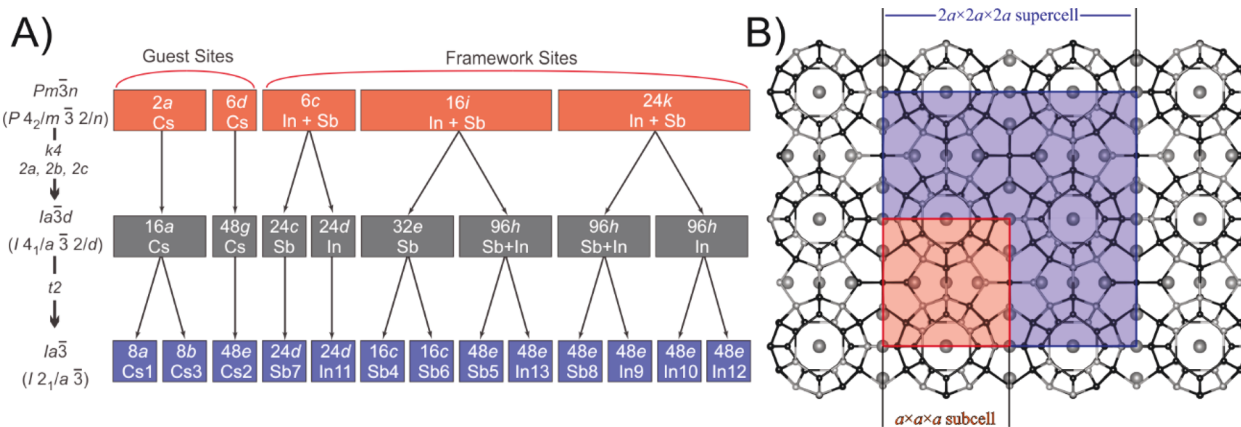


Figure 2. (A) Diagram showing the group-subgroup Wyckoff site splitting from the ideal type-I clathrate $Pm\bar{3}n$ subcell into the $Ia\bar{3}$ supercell for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$. (B) Projection of the clathrate superstructure with subcell and supercell emphasized in orange and blue.

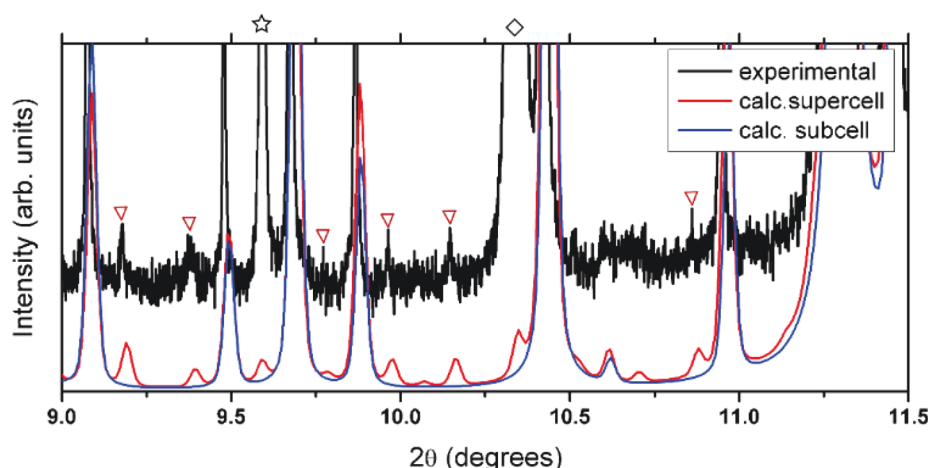


Figure 3. Region of high-resolution synchrotron PXRD pattern for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ sample collected at room temperature, $\lambda = 0.41275 \text{ \AA}$. Experimental data (black), calculated pattern for $Ia\bar{3}$ superstructure (red), and calculated pattern for $Pm\bar{3}n$ subcell (blue) are shown. Highlighted supercell reflections are denoted by red triangles, while reflections attributed to In and InSb impurity phases are shown as stars and diamonds, respectively. Note that the relative intensity of superstructural reflections does not exceed 0.15%.

0.95(1)–0.97(1) is expected to be In, while a site occupancy refinement that was close to unity within one esd would suggest Sb to be the correct atom type. This analysis was performed with multiple iterations stepwise for each of the 10 framework sites. After the sites were assigned and refined, the last step was to refine each site occupancy again to confirm they refined close to unity. The final model converges to positions with 100% occupancy within one esd and refined composition to be exactly $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$.

Our refinement is unable to distinguish a site that is 100% occupied by an atom of one type from the situation when the site is 90%/10% joint occupied by both In and Sb. There are two arguments supporting full 100% occupancy of each site by atom of one type: (i) an existence of the isostructural Ga-containing clathrates with full Ga/Sb ordering detected due to high scattering contrast of Ga and Sb (*vide infra*); (ii) an existence of the superstructural ordering. Indeed, a driving force for the superstructural ordering is a preference in chemical bonding, i.e., maximizing In–Sb and minimizing In–In and Sb–Sb interactions in the framework. Otherwise, mixed In/Sb sites can be realized in a primitive $Pm\bar{3}n$ clathrate subcell, similar to the case of $\text{Ba}_8\text{Cu}_{14}\text{Ge}_6\text{P}_{26}$,³³ in such clathrate framework a random mixture of In–Sb, In–Sn, and Sb–Sb interactions will be present. Four times increase of the primitive cell volume is only necessary for the complete segregation of In and Sb over a distinct framework sites to optimize chemical bonding in the clathrate framework. The predominant interactions present within the $Ia\bar{3}$ framework are In–Sb bonds, with a few In–In contacts, and finally only one Sb–Sb bond. In–Sb distances range between 2.802 and 2.893 Å with average In–Sb distance of 2.86 Å, slightly elongated compared with the sum of the two covalent radii (In–Sb, 2.81 Å; $r_{\text{In}} = 1.42 \text{ \AA}$; $r_{\text{Sb}} = 1.39 \text{ \AA}$)⁴³ but well in-line with distances reported for $\text{A}_2\text{In}_2\text{Sb}_3$ compounds.^{44–46}

The observed In–In distances range between 2.778 Å and 2.847 Å, agreeing well with the double covalent radius of In, 2.84 Å. These are slightly shorter than In–In distances in ternary Zintl phases, such as $\text{K}_{10}\text{In}_5\text{Sb}_9$ (2.92 Å) and $\text{Ba}_3\text{In}_4\text{Sb}_6$ (2.85 and 2.97 Å).^{47,48} The single Sb–Sb bond is 2.768 Å and is comparable to the double Sb covalent radius, 2.78 Å, but quite a bit shorter than the Sb–Sb interactions observed in

$\text{A}_2\text{In}_2\text{Sb}_3$ (2.86–2.88 Å) or the $[\text{Sb}@_{\text{In}_8}\text{Sb}_{12}]^{3-}$ and $[\text{Sb}@_{\text{In}_8}\text{Sb}_{12}]^{5-}$ clusters (2.81–2.85 Å).^{44–46,49}

Superstructural ordering of clathrate materials is caused by either (i) ordering of the framework or guest vacancies^{50–54} or (ii) preferences in the chemical bonding of the framework atoms with drastically different chemical nature.^{31,32,34,38,42,55,56} In the case of $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$, In and Sb distribution over the framework sites is coupled with a unit cell volume increase. This superstructure is a combination of *klassengleich* (*k4*) and *translationengleich* (*t2*) transformations.⁵⁷ For the unconventional transition metal clathrates, it has been shown that the nature of the observed clathrate ordering involves a preference in chemical bonding.³⁸ In the case of $\text{Ba}-\text{M}-\text{P}$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Zn}, \text{Au}$), site separation allows for the reduction or full elimination of M–M bonds within the framework.^{30–32,34,36,37} Examination of the In–Sb framework in $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ shows a similar trend, with the number of In–In and Sb–Sb bonds kept to a minimum while maximizing In–Sb interactions. Full elimination of In–In interactions, similar to the structure of binary InSb, is not possible as In contributes more than half of the atoms within the framework. Other clathrates, such as $\text{Cs}_8\text{Sn}_{44}\square_2$ or $\text{Ba}_8\text{Ge}_{43}\square_3$ (where $\square$ denotes Sn or Ge vacancy in the framework), exhibit only *klassengleich* *k4* transformation to the $Ia\bar{3}d$ space group through an ordering of the framework vacancies.^{50–53} $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ has an additional *translationengleich* *t2* transformation that further splits framework sites, indicating that $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ may need an additional type of ordering if certain interactions are to be reduced (e.g., In–In bonding). For instance, the splitting of the $Pm\bar{3}n$ 16i site eventually ends in discrete In and Sb sites in the $Ia\bar{3}$ clathrate structure that would not be possible in either $Pm\bar{3}n$ or $Ia\bar{3}d$ structures (Figure 2A).

Two single-crystal X-ray diffraction solutions for the $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ structure are presented: one collected in-house at 100 K and the other synchrotron-based at 10 K. The two solutions match quite well, with only small thermally induced deviations in observed distances. Previous low temperature clathrate studies in $\text{Ae}_8\text{Ga}_{16}\text{Ge}_{30}$ ($\text{Ae} = \text{Sr}, \text{Ba}, \text{Eu}$) showed that the guest position in the larger tetrakaidecahedron cage can split into many partially occupied positions around the cage.^{58–61} Refinement of the 10 K data set for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ does not show any displacement of Cs from the center of the

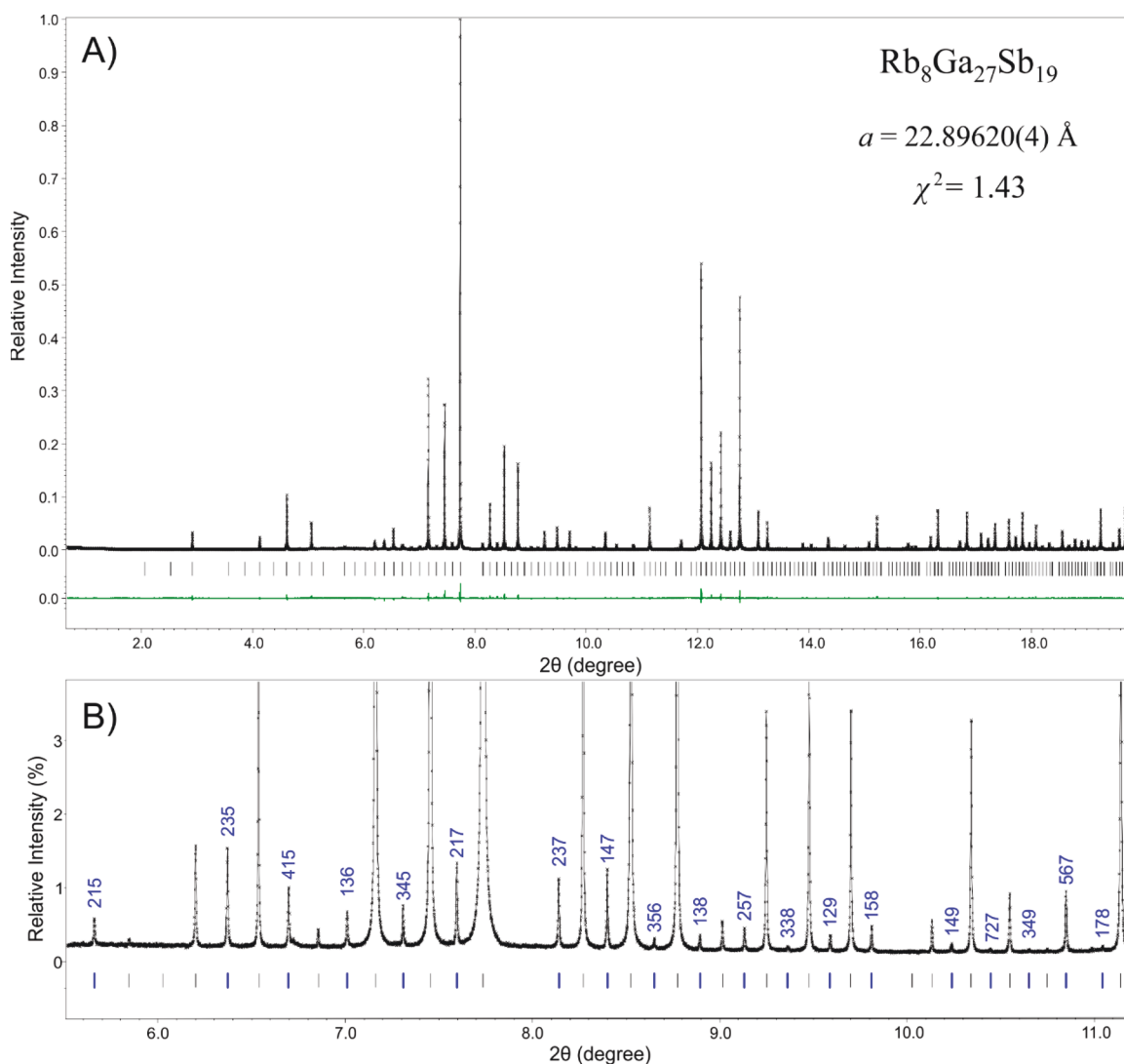


Figure 4. (A) PXRD pattern and corresponding Rietveld refinement (black line) of synchrotron powder X-ray diffraction data (black circles) for $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ collected at room temperature, $\lambda = 0.41275 \text{ \AA}$. Black ticks indicate the theoretical Bragg peak positions. The difference curve is shown in green at the bottom. (B) Fragment of the PXRD powder pattern with superstructural reflections tick marks and hkl indices highlighted in blue.

large cages, instead a flattening and expansion of the anisotropic parameters in the equatorial axis is shown.

Confirmation of the superstructure within bulk $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ samples was approached using high-resolution synchrotron PXRD. Small superstructural peaks are often hard to detect due to the low intensity caused by minute differences in Sb and In scattering factors. Peaks associated with the $Ia\bar{3}$ superstructure were observed throughout the PXRD pattern for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$, confirming that the superstructure is present throughout the bulk sample (Figure 3).

Crystal Structure of $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ and $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$. The crystal structures of the Ga analogues were difficult to establish using single-crystal diffraction due to heavy twinning of the studied crystals. For $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$, the reported model was achieved using in-house single crystal data with atomic displacement parameters for two framework sites fixed and not refined (Table S4). This model was validated by the refinement of synchrotron PXRD data. For $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$, no suitable crystals were found, and the crystal structure was established by means of Rietveld refinement of synchrotron PXRD data (Figure 4). The crystal structure of $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$

was used to generate the initial model. Final structural refinement corroborates that $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ is isostructural to $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ with the same superstructural ordering, $2a \times 2a \times 2a$ in the cubic $Ia\bar{3}$ space group. The intensity of the superstructural reflections is proportional to the difference in scattering factors of metal (Ga or In) and antimony. This is the reason why the superstructural reflections are extremely weak ($<0.15\%$) for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ (Figure 3). Due to the higher X-ray scattering contrast of Ga and Sb (atomic numbers 31 and 51), the reflections corresponding to the superstructural ordering are more intense in the case of $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ (Figure 4B). Additional refinement details and atomic coordinates for $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$ and $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ can be found in Tables S1, S4, and S5.

$\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ and $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$ are isostructural to $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$, crystallizing in the $Ia\bar{3}$ superstructure. Atomic segregation of Ga and Sb on the clathrate framework is obvious due to their distinct X-ray scattering coefficients. The Ga–Sb interactions in $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ ($2.649(1)$ – $2.726(2) \text{ \AA}$) and $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$ ($2.623(2)$ – $2.751(2) \text{ \AA}$) are slightly longer than those reported for Rb_2GaSb_2 (2.555 – $2.644 \text{ \AA}$),⁶² Cs_2GaSb_2

(2.550–2.599 Å),⁶³ and Cs_8GaSb_3 (2.608–2.676 Å).⁶⁴ The Ga–Ga bond distances in $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ and $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$ are similar, 2.471(2)–2.561(3) Å, which are longer than double covalent radius of Ga, 2.44 Å, but similar to Ga–Ga distance of 2.541 Å in $\text{Na}_2\text{Ga}_3\text{Sb}_3$.⁶⁵ The Sb–Sb interactions in $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ and $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$ are 2.709(1) and 2.745(3) Å, respectively. These distances are frequently observed in ternary antimonides such as $\text{EuFe}_4\text{Sb}_{12}$ (2.749 Å),⁶⁶ $\text{Ce}_{12}\text{Ge}_{5.2}\text{Sb}_{26.8}$ (2.619–2.797 Å),⁶⁷ and $\text{Eu}_{11}\text{Zn}_6\text{Sb}_{12}$ (2.795 Å).⁶⁸

Synthesis and Thermal Stability. The synthesis of $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ can be achieved by a stoichiometric reaction of the elements or through the use of binary precursors. All reactions must be performed within welded Ta ampules to offset the high vapor pressure of Cs at elevated temperatures. Homogenization of the samples made from elements is not fully achievable, even when applying multiple grinding and reannealing cycles, as admixtures of ductile In metal tend to segregate. To remedy this problem, a mixture of Cs and In metals and InSb in a ratio of 8:8:19 was used to improve the initial mixing and reactivity, reducing the amount of metallic In initially within the sample. The result was a nearly phase-pure sample of $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$, with only a small admixture of InSb present after three annealing cycles (Figure S1). Annealing temperatures higher than 823 K lead to formation of $\text{Cs}_2\text{In}_2\text{Sb}_3$ and Ta_3Sb admixtures.

In the case of $\text{A}_8\text{Ga}_{27}\text{Sb}_{19}$ ($\text{A} = \text{Rb}, \text{Cs}$) there was no detectable difference in the synthesis using stoichiometric reaction of the elements or via the aid of presynthesized binary GaSb precursors. The synthesis process of $\text{A}_8\text{Ga}_{27}\text{Sb}_{19}$ ($\text{A} = \text{Rb}, \text{Cs}$) samples were optimized using DSC data (Figure S2), indicating higher thermal stability for $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$, which decomposes around 1001(3) K, while $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ can only sustain heating up to 975(3) K. The final syntheses of $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$ and $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ were carried out at 973 and 943 K, respectively. After three annealings, gray uniform powder of $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ was collected without the presence of detectable Ga admixtures (Figure 4). Single-phase samples can be alternatively synthesized using a GaSb precursor. The $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$ compound has not been synthesized as a single-phase sample according to PXRD, but samples where $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$ was the main product were produced (Figure S3).

The as-synthesized samples of $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ do not initially appear to be air-sensitive, with no noticeable change in their PXRD within a few hours of air exposure. Nevertheless, SEM analyses reveals oxide formation on the surface of the material when only briefly exposed to ambient conditions. SEM performed in anaerobic conditions using an air-sensitive holder reveals no presence of oxides, indicating the oxides formed during brief air exposure. Submersion of $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ in water results in gas release and decomposition. Both $\text{A}_8\text{Ga}_{27}\text{Sb}_{19}$ samples were more sensitive to ambient conditions, with PXRD showing decomposition after 2 h of air exposure. Because of the relatively high humidity levels at ambient conditions, currently it is not clear whether the III–V clathrates are sensitive to air, humidity, or both.

Differential scanning calorimetry (DSC) was used to elucidate the thermal stability of $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ (Figures 5 and S4). Three endothermic peaks are visible in the heating curve, at 423, 850, and 943 K. The measured sample had a small admixture of In, which correlates well to the first peak ($T_{\text{melt}}(\text{In}) = 430 \text{ K}$). The next two peaks were assessed using *in situ* synchrotron PXRD studies on a sample containing $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ and admixtures of InSb and In (Figure 6). The

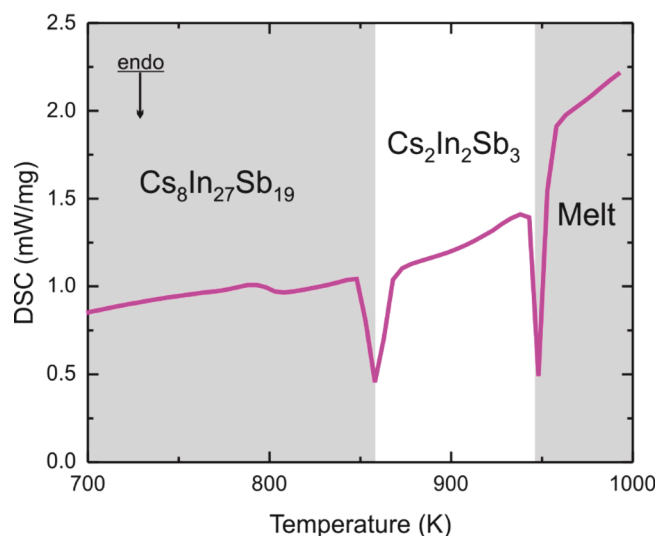


Figure 5. DSC heating curve for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$. The stability regions for different phases are highlighted.

InSb and In peaks begin to disappear at lower temperatures as expected, though InSb is slightly below its reported melting point of 799 K. Peaks assigned to $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ do not change until past 800 K, when they begin to change into peaks associated with $\text{Cs}_2\text{In}_2\text{Sb}_3$.⁶⁹ The full conversion is finished by 840 K. The melting of $\text{Cs}_2\text{In}_2\text{Sb}_3$ occurs at 952 K (data not shown). These data allow us to assign the first peak in Figure 5 to the decomposition of $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ and the second one to melting of $\text{Cs}_2\text{In}_2\text{Sb}_3$.

$\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$ exhibits one exothermic peak upon heating and a single endothermic peak during cooling, which corresponds to thermal decomposition (Figure S2) as evidenced by PXRD (Figure S5). $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ thermal behavior is similar to that of $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ (Figure S2), with two exothermic peaks at 961 and 975 K during the heating process, while only one endothermic peak was present upon cooling. After the DSC experiment, the sample of $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ was found to degrade into GaSb and a few unidentified peaks in the PXRD (Figure S5). Unlike the $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ clathrate, the two exothermic peaks of $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$ are very close to each other, less than 15 K apart; thus it is challenging to extract phase information within this small interval.

Density Functional Theory. The equilibrium lattice parameters, the formation energy, and the bulk modulus of novel III–V clathrates were computed by fitting the total energy as a function of volume on the Vinet equation of state.⁷⁰ The theoretical lattice parameters are in good agreement (1.7–2.6% larger) with those determined by X-ray diffraction (Table S7). $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ is softer than the Ga-containing clathrates, which feature ~25% larger bulk modulus. In the latter compounds, switching of the cation does not significantly affect either lattice parameter or bulk modulus.

Stability of III–V clathrates was probed by computing their energy with respect to the Hull curve, *i.e.* the energy of decomposition into the set of most stable materials for the given composition in the ternary phase diagram. According to the ternary phase diagram in Figure 7A, $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ decomposes into In, InSb, and $\text{Cs}_2\text{In}_2\text{Sb}_3$, agreeing well with experimental results. Computing the equation of states and total energy for all compounds in which clathrate would decompose shows that at zero temperature the energy of

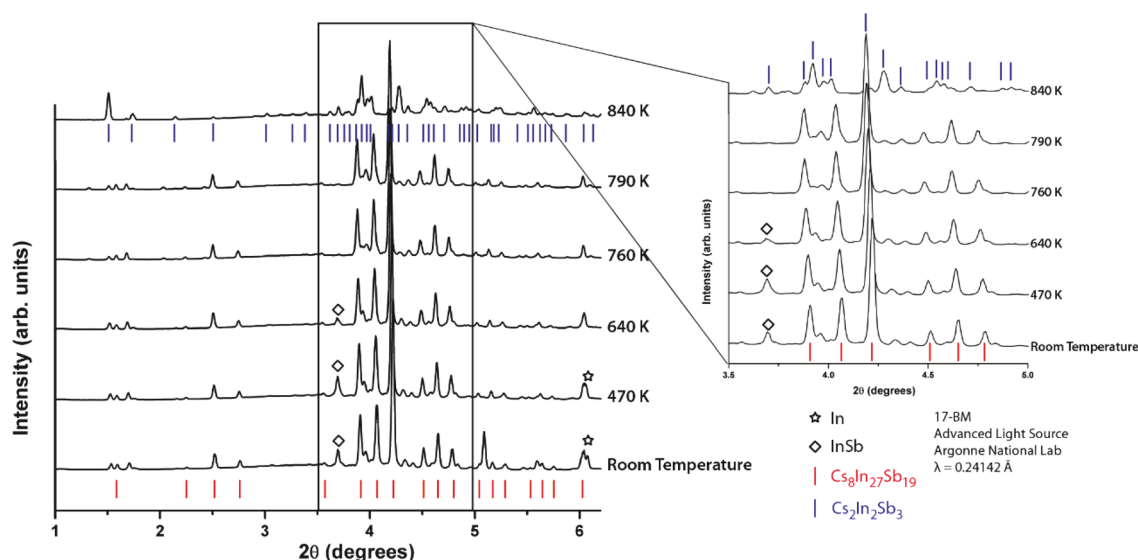


Figure 6. *In situ* variable temperature synchrotron PXRD of $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ sample, with a zoomed selected 2θ region shown ($\lambda = 0.24142 \text{ \AA}$). Admixtures of InSb and In are denoted by diamonds and stars, respectively. The sample was heated from room temperature (bottom pattern) to 840 K (top pattern). Calculated peak positions for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ and $\text{Cs}_2\text{In}_2\text{Sb}_3$ and are shown as red and blue thick lines, respectively.

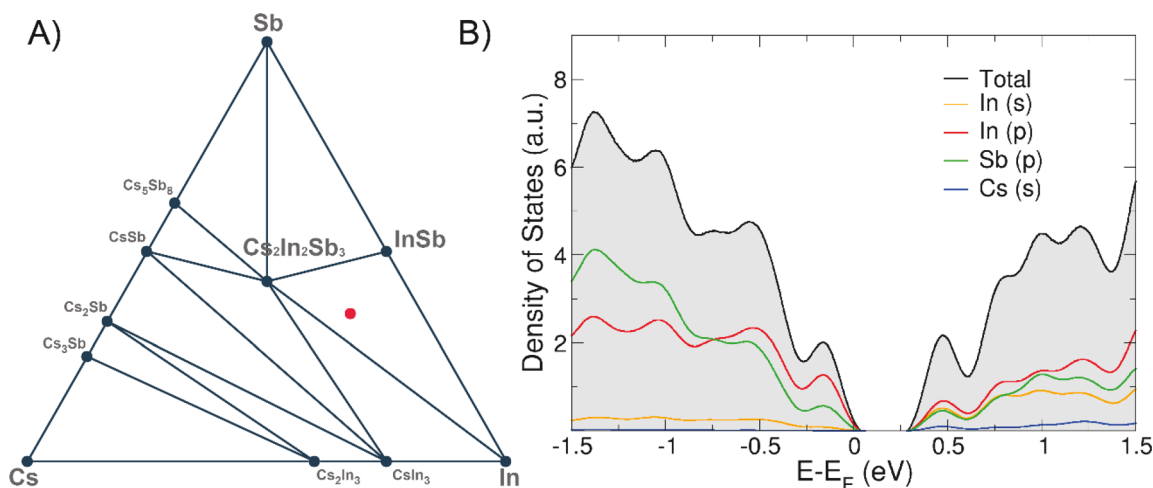


Figure 7. (A) Ternary phase diagram for the Cs–In–Sb system. The composition for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ is indicated by the solid red dot. (B) Calculated density of states for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$.

$\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ is 0.036 eV/atom below the Hull, indicating that the compound is stable at low temperature. The Ga-containing analogues are also stable against decomposition by 0.053 eV/atom (Cs–Ga) and 0.060 eV/atom (Rb–Ga).

$\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ (like $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$ and $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$) is an electron precise compound and thus a semiconductor. Its parent phase, InSb, is a direct band-gap semiconductor with a narrow gap of 0.24 eV (experimental).⁷¹ In DFT calculations, InSb appears semimetallic, with a vanishing gap at the Γ -point. This is a well-known shortcoming of DFT, which tends to systematically underestimate band gaps of III–V semiconductors with a mean relative error of $\sim 40\%$.⁷² Our DFT calculations predict that $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ is a semiconductor with a 0.34 eV indirect band gap. Notably, the direct transition at the H -point is close in value at 0.41 eV (Figure S11). A small density of Cs vacancies would make the material a p-type semiconductor and may be the origin of the positive Seebeck coefficient observed in the transport measurements (*vide infra*). The valence band density of states (DOS) of

$\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ (Figure 7B) is significantly steeper than that of InSb, leading to a high Seebeck coefficient as shown in experiments. Besides this marked difference, the DOS projected on the atomic wave function of the clathrate has a similar character to that of its parent InSb phase; i.e., the valence band is contributed by In- and Sb-5p states in $\sim 2:1$ ratio, while the conduction band is made of In-5s and -5p and Sb-5p states in almost equal amounts. The contribution of Cs states is negligible, indicating that Cs guest atoms completely donate their s electron to the clathrate structure. The curvature of the valence bands at the H -point is sufficient to provide small hole effective mass and thus high mobility (Figure S11). A full set of ternary phase diagrams, DOS, and tables of calculated parameters can be found in the Supporting Information (Figures S5–S13 and Table S7).

Transport Properties. Electronic and thermal transport measurements were performed on pelletized samples of the novel clathrates in the temperature regime of 10–300 K (Figure 8). All three compounds exhibit a typical dependence

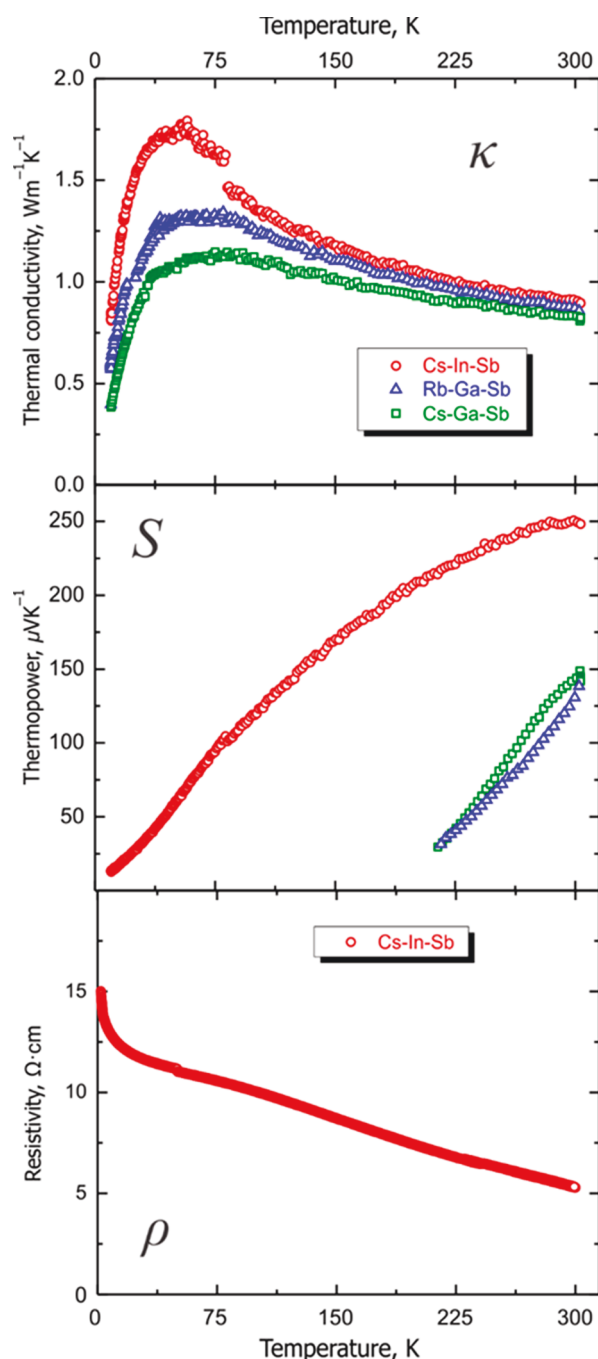


Figure 8. Transport properties of III–V clathrates: (top) thermal conductivity, (middle) Seebeck coefficient, and (bottom) electrical resistivity. $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$: red circles. $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$: green squares. $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$: blue triangles.

of the thermal conductivity for crystalline materials with a maximum around 50 K. For several Sn-based clathrates, glass-like behavior of the thermal conductivity was reported, which lacks this maximum at low temperature. This behavior was associated with the displacement of guest cations from the center of larger tetrakaidecahedral cages.^{73,74} Our 10 K single crystal diffraction experiment for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ exhibits no such displacement of Cs atoms, in accordance with the observed peak in the thermal conductivity at 50 K.

At room temperature, the thermal conductivity for all three compounds is comparable, 0.8–0.9 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ (Figure 8).

While low thermal conductivities of 1–3 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ are typical for conventional and transition metal clathrates,^{38,42,75} values below 1 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ were achieved only for clathrates containing heavy elements (Sn or Au) in the framework, such as $\text{Ba}_8\text{Au}_{16}\text{P}_{30}$ or $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$ with thermal conductivities below 0.7 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at room temperature.^{31,76–78} Large superstructural unit cells and the presence of heavy atoms in the framework are likely responsible for such ultralow values of the thermal conductivity. The electronic and lattice contributions to the thermal conductivity were extracted, showing a majority of the contribution coming from lattice transport (>99.9%).

$\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ exhibits p-type semiconducting behavior, with large positive Seebeck thermopower values of 250 $\mu\text{V}\cdot\text{K}^{-1}$ at 300 K (Figure 8). High Seebeck values and the ordered framework superstructure indicate that $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ is an electron precise compound, in good agreement with the calculated band structure. The curvature of the Seebeck curve appears as though it may be reaching a maximum near room temperature, before decreasing due to the bipolar effect (excitation of electrons into the conduction band), although the high-temperature measurements have not been performed to prove this. If the maximum is taken to occur at 300 K, a Goldsmid–Sharp band-gap estimation of $E_g = 2e|S_{\text{max}}|T_{\text{max}} = 0.15$ eV indicates a narrow-band gap for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$,⁷⁹ which is similar to the calculated band gap of 0.34 eV, taking into account accuracy of the band-gap prediction by DFT. Seebeck coefficients for the Ga-clathrates are lower, reaching 150 $\mu\text{V}\cdot\text{K}^{-1}$ at 300 K (Figure 8). Due to the high resistivity of Ga-containing compounds, the thermopower could only be measured in a limited temperature range. High values of the thermopower are not uncharted, with some tetrel-based p-type clathrates having shown similar values at room temperature ($\text{Ba}_8\text{Au}_{5.3}\text{Ge}_{40.7}$, 348 $\mu\text{V}\cdot\text{K}^{-1}$; $\text{Ba}_8\text{Ga}_{16}\text{Zn}_{3.2}\text{Ge}_{26.8}$, 250 $\mu\text{V}\cdot\text{K}^{-1}$; $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$, 150–370 $\mu\text{V}\cdot\text{K}^{-1}$).^{77,78,80,81}

Electrical resistivity of $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ decreases with temperature but did not show an exponential temperature dependence typical for conventional semiconductors. Resistivity almost linearly decreases in the 50–300 K range indicating heavily doped semiconducting behavior in line with the small band gap detected from thermopower measurements and computations (Figure 8). The room temperature resistivity value for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ of 5.3 $\Omega\cdot\text{cm}$ is slightly higher than that for other ternary triel-antimonides (KGaSb_2 , 2.0 $\Omega\cdot\text{cm}$; Ca_3AlSb_3 , 1.5 $\Omega\cdot\text{cm}$; Sr_3GaSb_3 , 0.5 $\Omega\cdot\text{cm}$; $\text{Cs}_5\text{Al}_2\text{Sb}_6$, 0.4 $\Omega\cdot\text{cm}$).^{82–86} No reliable electrical resistivity measurements were achieved for Ga-containing clathrate samples, presumably due to the high air-sensitivity of the samples resulting in surface oxidation.

The most intriguing property of these novel clathrates is hole mobility. As mentioned in the Introduction, for tetrel-based clathrates low mobilities have been reported, typically well below 50 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and one exceptional case of 170 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$.²⁵ By use of Hall measurements, the hole mobilities and concentrations were established for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$. Binary InSb has a high hole carrier mobility of $\sim 800\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and room temperature hole concentrations ranging from $\sim 10^{15}$ to 10^{16} cm^{-3} .^{87,88} The complex clathrate $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ inherits such properties with similar mobility and concentration values, 880 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and $1.42 \times 10^{15}\text{ cm}^{-3}$. This is dissimilar to other reports of p-type ternary compounds containing III–V fragments, such as in the supertetrahedral layered compounds $\text{Ae}_5\text{Tr}_{22}\text{As}_{32}$ and $\text{Ae}_3\text{Ga}_6\text{As}_8$ (Ae = Sr, Eu; Tr = Ga, In), in

which there is a substantial decrease in mobility down to $0.2\text{--}98\text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ going from the binary to ternary compounds.⁸⁹ High hole mobility within bulk samples at room temperature is uncommon but can still be found in some compounds, such as doped CsBi_4Te_6 ($700\text{--}1000\text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$), CoP_3 ($748\text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$), or CoSb_3 ($1500\text{--}2970\text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$).^{90–92} The ordered nature of the In–Sb framework may be a key to the high mobility of $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$. It was shown that defects may significantly affect the electronic and optical properties of III–V semiconductors.⁵

Obtaining high mobility in clathrates has enormous potential because of their tunability. In binary III–V semiconductors, aliovalent doping is used to modify carrier concentration and band structure to affect the electronic properties. Such doping is limited to a ppm concentration level of dopants. In the case of clathrates, aliovalent substitution was shown to be effective not only in adjusting the carrier concentration and type but also in inducing metal-to-semiconductor transitions. For example, $\text{Ba}_8\text{Cu}_{16}\text{P}_{30}$ clathrate exhibited multiple metal-to-semiconductor transitions upon replacement of the part of Cu atoms with Zn.^{34,35,37} Thus, aliovalent substitution in III–V clathrates opens ways to designing materials with high mobility and tunable carrier concentrations, which is desirable for optoelectronic and thermoelectric applications. The stability of the III–V clathrate can be improved by introducing stronger covalent bonds in the framework, for example, by increasing the electronegativity difference between group 13 metal and pnictide. In–Sb and Ga–Sb based clathrates reported here open a window of possibilities for designing functional materials based on clathrates with intrinsically high mobility. Moreover, this discovery indicates that other binary semiconductors, for example, II–VI, can be converted into clathrates using proper design principles.

CONCLUSION

The first examples of fully main group tetrel-free unconventional clathrates, $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$, $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$, and $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$, are presented. These clathrates crystallize in a $Ia\bar{3}$ superstructure of the type-I clathrate, with the framework elements segregating into individual sites. A combination of high-resolution synchrotron powder and single-crystal X-ray diffraction was utilized to elucidate the structures. High-resolution PXRD indicates that the structural ordering is present throughout the bulk sample. DFT calculations show that all clathrates are energetically stable semiconductors with bandgaps ranging from 0.34 to 0.81 eV. Basic thermal and charge transport properties were characterized for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$, $\text{Cs}_8\text{Ga}_{27}\text{Sb}_{19}$, and $\text{Rb}_8\text{Ga}_{27}\text{Sb}_{19}$, showing low thermal conductivity, ranging between 0.8 and $0.9\text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at room temperature. The clathrates exhibit p-type semiconducting behavior, with high thermopower values of $250\text{ }\mu\text{V}\cdot\text{K}^{-1}$ (In) and $150\text{ }\mu\text{V}\cdot\text{K}^{-1}$ (Ga) at 300 K. Hall measurements for $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ show a carrier concentration of $1.4\times 10^{15}\text{ cm}^{-3}$ and extraordinary hole mobility of $880\text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ at 300 K. The mobility of the novel $\text{Cs}_8\text{In}_{27}\text{Sb}_{19}$ clathrate is on par with those for one of the best binary semiconductors, InSb, making the discovery of III–V clathrates quite intriguing as many III–V binary semiconductors have been studied and used in high-profile electronic applications. High tolerance of unconventional clathrates to aliovalent substitutions allows for tuning of carrier concentration in a wide range, which is a desirable property for high mobility semiconductors. Whether other

types of simple binary semiconductors, i.e., II–VI, can be converted into clathrates is currently under investigation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.9b12351>.

Experimental details, figures, and tables pertinent to characterization techniques used: powder and single crystal X-ray diffraction, energy dispersive X-ray spectroscopy, differential scanning calorimetry, spark plasma sintering, transport property measurements, electronic structure calculations, bands and DOS diagrams, and calculated ternary phase diagrams (PDF)

Crystallographic information (CIF)

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Notes

The authors declare no competing financial interest.

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