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Complex Disorder in Type-I Clathrates: Synthesis and Structural Characterization of $A_8Ga_xSn_{46-x}$ ($A = Rb, Cs; 6.9 < x < 7.5$)

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Abstract: Exploratory studies in the systems Rb–Ga–Sn and Cs–Ga–Sn yielded the cubic type-I clathrates with refined compositions $Rb_8Ga_xSn_{46-x}$ and $Cs_8Ga_xSn_{46-x}$ ($6.9 < x < 7.5$). Nearly single-phase materials with good crystallinity were obtained from stoichiometric reactions of the elements. The structures were characterized by means of single-crystal X-ray diffraction methods. Both $Rb_8Ga_xSn_{46-x}$ and $Cs_8Ga_xSn_{46-x}$ represents cases, where a Group 13 element randomly substitutes a Group 14 element in the structure. The extent of Ga/Sn mixing is apparently governed by the drive of the system to achieve an optimal valence electron count, and hence, $Rb_8Ga_xSn_{46-x}$ and $Cs_8Ga_xSn_{46-x}$ ($x \approx 8$) can be regarded as Zintl phases. This notion is supported by structure refinements on a multitude of single-crystal X-ray diffraction data, which also confirm that both types of cages in the cubic type-I structure are fully occupied by Rb and Cs atoms. The open-framework, comprised of 46 nodes per formula unit, adapts to the incorporation of nearly eight Ga atoms within the matrix of Sn, whereby small, short-range distortions result. The exact nature of these effects is still unclear, as so far, the structural variations could only be modeled as both positional and occupational disorder at one of three framework sites. Since vacancies in the structures of the binary type-I clathrates $A_8Sn_{46-x}\square_x$ ($A = Rb, Cs; \square =$ missing Sn atom) are also known to cause local distortions, the latter were also synthesized with the same protocols used for the synthesis of $A_8Ga_xSn_{46-x}$ and structurally re-analyzed. The results from the latter studies confirm that homogeneity issues abound, and that the final structures/compositions are an intricate function of the experimental conditions.

Keywords: clathrates; type-I structure; Zintl phases; crystal structures

1. Introduction

In the past two to three decades, thermoelectric materials have played an important role in the development of new technologies for primary power generation and solid-state energy conversion. Such materials are capable of converting waste heat into electricity, which may be useful for a vast amount of applications. Due to the current inefficiency of such technologies, the discovery of new, and optimization of known, materials is essential to making thermoelectric devices a part of everyday life. Among prospective materials for thermoelectric applications, intermetallic clathrates are of particular interest due to their unique structures and properties [1]. Such compounds, with host–guest type interactions, have been known for a while, whereas isotypic compounds based on the elements of Group 14 have only been known since the 1960s [2–4]. Silicon, germanium, and tin form the host framework, which can be partially substituted by elements of Group 13, late transition metals or Group 15 elements. The framework boasts large cages, which are capable of encapsulating guest atoms, such as alkali metals, alkali-earth metals or even divalent (Eu) and trivalent rare-earth metals [5–7]. Intermetallic

clathrates readily satisfy conditions for the important “phonon-glass electron-singe-crystal” concept for thermoelectrics, introduced by Slack [8]. The vibrations of the guest atoms in the large cages, also known as “rattling”, lower the lattice thermal conductivity, whereas the inflexible framework with mostly covalent interactions between host atoms arranges high electron mobility. Therefore, high thermoelectric performance may be achieved for such intermetallic clathrates.

The synthesis and characterization of new intermetallic clathrate phases has been a focus area of research for many groups [2,3,9–13]. Our group has also been involved in these topics, and in the last several years, we have identified several unique type-I and type-II clathrates [14–18]. Surveying the literature, one finds that the most common structure, among intermetallic clathrates, based on Group 14 elements, is the type-I structure, shown in Figure 1.

Figure 1. Schematic view of the primitive-centered cubic clathrate type-I structure (space group $Pm\bar{3}n$). Color coding for the electronic version of the paper: pentagonal dodecahedra are red (darker), tetrakaidecahedra are yellow, and guest atoms are blue.

Type-I crystallizes in the primitive cubic space group $Pm\bar{3}n$ (No. 223) and has the general formula of A_8M_{46} (A denotes guest atom and M denotes framework atoms, respectively). Such a formula represents a binary composition without any defects, vacancies or mixed-occupied sites. The structure of the type-I clathrates can be characterized by the existence of 20-vertex pentagonal dodecahedra and 24-vertex tetrakaidecahedra, constituted by the abovementioned M -atoms. The guest A -atoms occupy the $2a$ sites inside the 20-vertex cage and the $6d$ sites in the 24-vertex cages. However, fractional occupation of the cages by guest atoms, missing framework atoms (i.e., vacancies), or substitutional disorder on the framework sites are very common and is a recurring theme in the structural chemistry of type-I clathrates [3]. These traits have been described and systematized earlier in several articles and books [2,5,9,12].

In the context of this manuscript, a brief description of the type-I clathrates containing alkali metals as the guest atom and mixed Group 13/14 elements as the host atoms is required. Substitutional disorder on the framework sites, where atoms of Group 14 elements (Si , Ge , or Sn = Tetrel or Tt , hereafter) are replaced by atoms of Group 13 elements (Al , Ga , or In = Triel or Tr , hereafter), has been well studied [3]. Such disorder is characterized by a site preference for the framework side with the lowest multiplicity, $6c$ (vide infra), since this ensures the avoidance of energetically unfavorable bonding between substituting atoms of the Tr -elements. In that sense, the site occupancy factor (s.o.f.) for the $6c$ site can even reach as high as 100% [3]. From a standpoint of an optimized electronic structure, the formula $A_8Tr_8Tt_{38}$ ($A = \text{Na–Cs}$, $Tr = \text{Al–Ga}$, $Tt = \text{Si–Sn}$) represents the idealized composition for such a ternary phase, where all atoms achieve an electron count conforming to the Zintl-Klemm

concept [19]. Therefore, *Tr–Tt* substitutions are occurring not only on the 6c site, but also to a much smaller extent on 16i and 24k sites.

Most of the known ternary Sn-bearing type-I clathrates are based on the late transition elements of Group 12 [18,20–23], whereas structural studies of compounds in the *A–Tr–Sn* systems (*A* = Na–Cs; *Tr* = Al–Ga) are limited to only several examples [17,20,24–31]. Importantly, the published studies do not cover all possible members of this potentially much larger clathrate family, which can be extended even more by considering the possibility for ordering of different types of guest atoms in the quaternary compositions [14,15,24,32,33].

This study focuses on the structural aspects of the clathrate type-I phases with balanced compositions close to $\text{Rb}_8\text{Ga}_x\text{Sn}_{46-x}$ ($x = 6.9(1)–7.1(1)$) and $\text{Cs}_8\text{Ga}_x\text{Sn}_{46-x}$ ($x = 7.5(1)$). Some structural data on $\text{Rb}_8\text{Ga}_8\text{Sn}_{38}$ and $\text{Cs}_8\text{Ga}_8\text{Sn}_{38}$ phases have been already reported by Kröner, von Schnering, and Nesper in 1998, but ICSD records are missed [30,31]. The related compound $\text{K}_8\text{Ga}_8\text{Sn}_{38}$ has its structure and properties established already [27], and is therefore not included in the current discussion. Since the structural work we present here provides evidence for rare positional and occupational disorder at one of three framework sites, suggestive of the fact that the final structure/composition are dependent on the experimental conditions, we also provide another look at the structures of the binary type-I clathrates $\text{A}_8\text{Sn}_{44}\square_2$ (*A* = Rb, Cs; $\square$ = missing Sn atom), which have been previously studied [34,35].

2. Materials and Methods

2.1. Synthesis

All manipulations were performed inside an argon-filled glovebox with oxygen and moisture levels of less than 1 ppm or under vacuum, due to the air sensitivity of the reactants. Starting materials with a nominal purity of greater than 99.9 wt. % were purchased from Alfa Aesar or Sigma-Aldrich.

Originally, we were not interested in the ternary $\text{A}_8\text{Ga}_8\text{Sn}_{38}$ compositions (*A* = K, Rb, Cs); they were found as a major product in the direct reactions performed in Nb-tubes with nominal *A*:Eu:Ga:Sn ratios of 6:2:10:36. These experiments were set up with the idea of synthesizing Sn-analogs of the clathrates $\text{K}_6\text{Eu}_2\text{Ga}_{10}\text{Ge}_{36}$ and $\text{Rb}_6\text{Eu}_2\text{In}_{10}\text{Ge}_{36}$ [7,32], where alkali metal atoms and Eu atoms are nearly ordered in the two different cages—the 24-vertex tetrakaidekahedra and the 20-vertex pentagonal dodecahedra, respectively. After the structures of the major product of these experiments were established by single-crystal X-ray diffraction methods and proven to be free of rare-earth elements, new batches of reactions between *A*, Ga, and Sn in the ratios 7–8:7–9:37–39. These syntheses were also performed in Nb-tubes, which, following the insertion of the elements into them, were arc-welded and shut-closed. The Nb-tubes were subsequently enclosed in fused silica ampoules, which were evacuated and flamed-sealed.

The reactions were carried out in programmable muffle furnaces. Several different heat-treatment protocols were employed. The first one was as follows: ramp to 1243 K, (rate = $100\text{ K}\cdot\text{h}^{-1}$), homogenization at 1243 K for 1h, cooling to 823 K (rate = $100\text{ K}\cdot\text{h}^{-1}$), isothermal anneal at 823 K for 100 h, cooling to room temperature (rate = $5\text{ K}\cdot\text{h}^{-1}$). The second one was as follows: ramp to 873 K (rate = $100\text{ K}\cdot\text{h}^{-1}$), anneal for 15 days at this temperature and then cool slowly with a rate $5\text{ K}\cdot\text{h}^{-1}$. After the completion of the heat treatment, the Nb-tubes were brought back into the glovebox and opened. The reactions produced visually homogeneous samples of small, but well-defined crystals with cubic/cube-octahedral morphology and metallic luster. Here, it is important to note that the refined compositions from single-crystal X-ray diffraction work are $\text{Rb}_8\text{Ga}_x\text{Sn}_{46-x}$ and $\text{Cs}_8\text{Ga}_x\text{Sn}_{46-x}$ ($6.9 < x < 7.5$), i.e., slightly different from the loaded compositions. No evidence was found that compounds with the idealized $\text{A}_8\text{Ga}_8\text{Sn}_{38}$ (*A* = Rb, Cs) formula, or Ga-rich compounds $\text{A}_8\text{Ga}_x\text{Sn}_{46-x}$ ($x > 8$) can be prepared.

The set of several binary $\text{A}_8\text{Sn}_{46-x}\square_x$ (*A* = Rb, Cs; $x \approx 2$) phases was received in attempts to synthesize rare-earth metal substituted ternary phases by direct reactions between *A*, *RE*, Sn in the ratios 2:1:8–10 (*A* = Rb, Cs; *RE* = La–Nd, Sm, Gd–Yb). The heat-treatment protocols were as described above.

The tubes were brought back into the glovebox after reactions were completed, and opened. In case of the A-Ga-Sn system, the main solid products were well-formed single crystals of $\text{Rb}_8\text{Ga}_{7.1(1)}\text{Sn}_{38.92}$ and $\text{Cs}_8\text{Ga}_{7.5(1)}\text{Sn}_{38.50}$. However, refined Ga:Sn ratios were always different from the loaded composition, but close to the idealized $\text{A}_8\text{Ga}_8\text{Sn}_{38}$ ($A = \text{Rb}, \text{Cs}$) formula.

2.2. Powder X-Ray Diffraction (PXRD)

The reaction products were ground using an agate mortar and pestle and the polycrystalline materials were analyzed with a Rigaku Miniflex diffractometer ($\text{Cu K}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$, Rigaku, Japan) operating inside a nitrogen-filled glovebox. Data were collected in a θ – θ mode between 10° and 65° with a step size of 0.05° and 2s/step counting time. The collected data were used for phase identification and qualitative assessment of the phase purity. The title compounds appear to be air-stable according to the PXRD results. Traces of elemental β -Sn were found in all cases. A representative PXRD pattern is presented in Figure S1.

2.3. Single-Crystal X-Ray Diffraction (SCXRD)

Selected single crystals of good quality were carefully picked from the reaction product. X-ray single-crystal data were collected on a Bruker APEX-II CCD diffractometer (Bruker AXS, Germany) equipped with $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 200(2) K and integrated with the Bruker SAINT software package [36]. Data were corrected for absorption effects by using the multi-scan absorption correction method with the SADABS program [37]. Crystal structures were solved using SHELXT and refined by full-matrix least-squares method on F^2 using SHELXL [38,39]. The atomic labels and the coordinates were standardized with the STRUCTURE TIDY program [40]. Details of the data collection, atomic coordinates, and selected interatomic distances for representative samples are given in Tables 1–3. CSD contains relevant crystallographic data for this paper, which can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

Table 1. Selected crystal data and structure refinement parameters for $\text{Rb}_8\text{Ga}_{7.1(1)}\text{Sn}_{38.9}$ and $\text{Cs}_8\text{Ga}_{7.5(1)}\text{Sn}_{38.5}$; Space Group $Pm\bar{3}n$ (No. 223); $Z = 1$; $T = 200(2) \text{ K}$; $\text{Mo K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$.

Compound	$\text{Rb}_8\text{Ga}_{7.1(1)}\text{Sn}_{38.9}$ ²	$\text{Cs}_8\text{Ga}_{7.5(1)}\text{Sn}_{38.5}$
fw/g mol ^{−1}	5797.23	6156.24
a/Å	11.9691(3)	12.023(2)
V/Å ³	1714.69(13)	1737.8(9)
$\rho_{\text{calc.}}/\text{g cm}^{-3}$	5.613	5.882
μ/cm^{-1}	222.39	205.19
$R_1 (I > 2\sigma(I))$ ¹	0.0151	0.0168
$wR_2 (I > 2\sigma(I))$ ¹	0.0328	0.0334
$R_1 (\text{all data})$ ¹	0.0183	0.0209
$wR_2 (\text{all data})$ ¹	0.0334	0.341
$\Delta\rho_{\text{max\&min}}/\text{e}^{-}\text{\AA}^{-3}$	0.50 & −0.59	0.56 & −0.56

¹ $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum [w (F_o^2 - F_c^2)^2] / \sum [w (F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (A \cdot P)^2 + (B \cdot P)]$, and $P = (F_o^2 + 2F_c^2)/3$; A and B weight coefficients. The corresponding CIFs have been deposited and have deposition numbers CSD 1989526–1989527;² Another dataset with refined formula of $\text{Rb}_8\text{Ga}_{6.9(1)}\text{Sn}_{39.1}$ and unit cell parameter of 11.9704(3) (CSD number 1989528).

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters $U_{eq}(\text{\AA}^2)$ ¹ for $\text{Rb}_8\text{Ga}_{7.1(1)}\text{Sn}_{38.9}$ and $\text{Cs}_8\text{Ga}_{7.5(1)}\text{Sn}_{38.5}$.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}(\text{\AA}^2)$ ¹
Rb1	6 <i>d</i>	$\frac{1}{4}$	$\frac{1}{2}$	0	0.041(1)
Rb2	2 <i>a</i>	0	0	0	0.017(1)
Sn1/Ga1 ²	24 <i>k</i>	0	0.3119(1)	0.1179(1)	0.014(1)
Sn2/Ga2 ²	16 <i>i</i>	0.18337(2)	<i>x</i>	<i>x</i>	0.014(1)
Sn3/Ga3 ²	6 <i>c</i>	$\frac{1}{4}$	0	$\frac{1}{2}$	0.016(1)
Cs1	6 <i>d</i>	$\frac{1}{4}$	$\frac{1}{2}$	0	0.028(1)
Cs2	2 <i>a</i>	0	0	0	0.013(1)
Sn1 ³	24 <i>k</i>	0	0.3114(1)	0.1179(1)	0.015(1)
Ga1 ³	24 <i>k</i>	0	0.3493(12)	0.1345(8)	0.015(1)
Sn2/Ga2 ⁴	16 <i>i</i>	0.18340(2)	<i>x</i>	<i>x</i>	0.014(1)
Sn3/Ga3 ⁴	6 <i>c</i>	$\frac{1}{4}$	0	$\frac{1}{2}$	0.014(1)

¹ U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor; ² Refined occupancies according to refinement: Sn1/Ga1 = 0.858(11)Sn1 + 0.142Ga1; Sn2/Ga2 = 0.933(12)Sn2 + 0.067Ga2; Sn3/Ga3 = 0.562(14)Sn3 + 0.438Ga3; ³ Positional disorder, modeled as a major site of Sn1 = 0.884(6) and a minor site of Ga1 = 0.116; ⁴ Refined occupancies according to refinement: Sn2/Ga2 = 0.945(8)Sn2 + 0.055Ga2; Sn3/Ga3 = 0.361(11)Sn3 + 0.639Ga3.

Table 3. Selected interatomic distances (Å) for $\text{Rb}_8\text{Ga}_{7.1(1)}\text{Sn}_{38.9}$ and $\text{Cs}_8\text{Ga}_{7.5(1)}\text{Sn}_{38.5}$. *M* denotes the mixed occupied Sn/Ga position.

$\text{Rb}_8\text{Ga}_{7.1(1)}\text{Sn}_{38.9}$	<i>d</i> /Å	$\text{Cs}_8\text{Ga}_{7.5(1)}\text{Sn}_{38.5}$	<i>d</i> /Å
M1–M1	2.8235(7)	Sn1/Ga1–Sn1	2.8342(19)/3.069(11)
M1–M2 (×2)	2.7925(2)	Sn1/Ga1–M2 (×2)	2.8015(8)/3.031(9)
M1–M3	2.7504(3)	Sn1/Ga1–M3	2.7688(15)/2.282(15)
M2–M1 (×3)	2.7925(2)	M2–Sn1/Ga1 (×3)	2.8015(8)/3.031(9)
M2–M2	2.7626(8)	M2–M2	2.7736(10)
M3–M1 (×4)	2.7504(3)	M3–Sn1/Ga1 (×4)	2.7688(15)/2.282(15)
Rb1–M1 (×8)	4.0016(2)	Cs1–Sn1/Ga1 (×8)	4.0234(9)/3.864(6)
Rb2–M1 (×12)	3.9916(3)	Cs2–Sn1 (×12)	4.0027(16)
Rb2–M2 (×8)	3.8014(4)	Cs2–M2 (×8)	3.8192(8)

3. Results and Discussion

The title clathrates were synthesized with a high level of crystallinity from direct reaction of the elements, as described in the Materials and Methods section. One can notice several differences pertaining to the synthesis in the *A–Tr–Sn* systems, compared to *A–Tr–Si* and *A–Tr–Ge* systems. First, is the ability to perform the reaction at moderate temperatures (873 K), which is attributed to the low melting points of all starting materials (not the case for Ge and Si, in particular). The second aspect, which is related to the first, is the relative stability of the Nb containers in the processes involving Sn, unlike the risk accompanying the formation of Nb-bearing germanides and silicides [41].

Applying the self-flux method to grow sizeable single crystals was not explored as part of this study; however, other works have demonstrated the feasibility of this approach [18]. An alternative flux-growth technique calls for using the metal halides as a modified flux medium, might also be suggested as means to obtain bulk samples with good crystallinity [42]. These could be beneficial for studying the physical properties of $\text{Rb}_8\text{Ga}_x\text{Sn}_{46-x}$ and $\text{Cs}_8\text{Ga}_x\text{Sn}_{46-x}$ ($x \approx 8$); however, the lesson learned from the present studies of the crystal chemistry of the title clathrate phases is that the outcomes of the synthesis are very much dependent on the reaction conditions. Additionally, the chemical formulae of the products are not always identical to the loaded compositions, which will be especially true for flux reactions. This is not to say that the reactions suffer from poor reproducibility, rather the opposite—reproducibility is excellent, as judged by different batches, with different nominal compositions, which consistently yields products with matching unit cell volumes and only slightly different formulas. Thus, one can argue the information from the published crystal structures ought to

be used with caution, and that single-crystal X-ray diffraction work (or Rietveld refinements if dealing with polycrystalline materials) should be employed to verify the received final structures/compositions.

The initial idea of the synthesis was to incorporate Europium into the clathrate cage as an extension of the work on $\text{Rb}_{8-x}\text{Eu}_x(\text{In,Ge})_{46}$ clathrates performed previously by our group [32], which proved unsuccessful (vide supra). The co-existence of both alkali metals and alkaline-earth metals, or Eu, is known for the different type-I clathrates, such as $\text{K}_6\text{AE}_2\text{M}_5\text{Ge}_{41}$ ($\text{AE} = \text{Eu, Ba}$; $\text{M} = \text{Zn, Cd}$) and $\text{K}_6\text{Eu}_2\text{Ga}_{10}\text{Ge}_{36}$ [7,33]. Apparently, ordering of chemically different guest atom in Sn-bearing clathrates is also possible, as demonstrated for the type-II clathrate $\text{Cs}_8\text{Ba}_{16}\text{Ga}_{40}\text{Sn}_{96}$ [43]; however, Eu might not be the right size-match to allow for that. Circumstantial evidence in support of this conjecture includes the mixed guest atom type-I clathrates $\text{K}_{1.58}\text{Cs}_{6.42}\text{Sn}_{44.02}$, $\text{Rb}_x\text{Cs}_{8-x}\text{Sn}_{44}\square_2$ [44,45], which show the tendency for the larger Cs to fill the larger 24-vertex cages, while the smaller Rb and K, in particular, are better suited for the smaller 20-vertex cage (Figure 2). The report on $\text{K}_{7.1}\text{Ba}_{0.3}\text{Ga}_{8.3}\text{Sn}_{37.7}$ shows that it is possible to have Sn-bearing clathrates with guest atoms from Groups 1 and 2, where Ba occupies only one (2a) site [24].

Figure 2. Fragments of the structure of (a) $\text{Rb}_8\text{Ga}_{7.1(1)}\text{Sn}_{38.9}$ and (b) $\text{Cs}_8\text{Ga}_{7.5(1)}\text{Sn}_{38.5}$. Sn1/Ga1 (Sn1 for $\text{Cs}_8\text{Ga}_{7.5(1)}\text{Sn}_{38.5}$), Sn2/Ga2, Sn3/Ga3, (Ga1 for $\text{Cs}_8\text{Ga}_{7.5(1)}\text{Sn}_{38.5}$) atoms are drawn as plum, orange, green, and light blue respectively. Displacement ellipsoids for guest atoms Rb and Cs atoms (blue) are shown at the 95% probability.

The somewhat limited success with making Sn-clathrates with different guest atoms might be attributed to the presence of very large cages, largest among the Group 14 clathrates, thereby limiting the choice of “filler” atoms. In that context, we also note that it is not surprising to have Si-clathrates in which the cages are smaller, and are not fully occupied by the guest atoms [42,46]. Our work did not yield at any clues that in $\text{Rb}_8\text{Ga}_x\text{Sn}_{46-x}$ and $\text{Cs}_8\text{Ga}_x\text{Sn}_{46-x}$ ($x \approx 8$) could be vacancies on the alkali metal sites. Occupancies of the 2a and 6d sites were checked by freeing the occupation factor of an

individual atom and in all cases were found to be very close to 1 (within 3–4 e.s.d.s). The same type of observation was made with regard to the ternary type-I clathrates $A_8Al_xSn_{46-x}$ ($A = K, Rb; x \approx 8$) [17].

Along the same line of thought, another interesting parallel can be drawn between $A_8Ga_xSn_{46-x}$ ($A = Rb, Cs; x \approx 8$) and $A_8Al_xSn_{46-x}$ ($A = K, Rb; x \approx 8$). During these studies, we noticed that attempts at making $Cs_8Al_xSn_{46-x}$ were unsuccessful. The product of such reactions appeared to be unreacted Al and binary $Cs_8Sn_{44}\square_2$. Apparently, there are subtle differences between the Sn–Al and Sn–Ga clathrates, which are not captured by the discussion on atomic sizes and formal charges. There must be a different reason that makes the formation of a clathrate phase in the Cs–Al–Sn systems energetically unfavorable, and the origin of such effect remains unknown. We speculate that the unique positional and occupational disorder in $Cs_8Ga_xSn_{46-x}$ ($x \approx 8$), which was modeled by a split Sn (24k) position, might be a contributing factor, but this hypothesis requires further testing. It might be worthwhile to investigate $Cs_8In_xSn_{46-x}$ ($x \approx 8$), although differentiation of the In and Sn atoms by conventional X-ray crystallography is expected to be very challenging.

The diffraction patterns for both $Rb_8Ga_xSn_{46-x}$ and $Cs_8Ga_xSn_{46-x}$ ($x \approx 8$) (Figure S1) indicate that they crystallize in the average type-I structure (Tables 1–3). For simplicity, the formulae above and $Rb_8Ga_8Sn_{38}$ and $Cs_8Ga_8Sn_{38}$ will be used interchangeably throughout the manuscript. It is worthwhile to mention here that the unit cell parameter of the ternary $Rb_8Ga_8Sn_{38}$ phase is 11.9691(3) Å, which is significantly smaller than that for the binary Rb_8Sn_{44} ($a \approx 12.04$, Table 4). A similar observation can be made for the Cs-bearing compound too. While these findings are not surprising, and can be easily rationalized as being due to the smaller atomic radius of Ga (1.26 Å) compared to Sn (1.40 Å), comparison of the unit cell parameters of $Rb_8Al_8Sn_{38}$ and $Rb_8Ga_8Sn_{38}$ presents an argument that there is more than meets the eye here. The unit cell parameter of $Rb_8Al_8Sn_{38}$ is 12.011(7) Å, an intermediate value between those of $Rb_8Ga_8Sn_{38}$ and Rb_8Sn_{44} . Taking into account the above, in the context of the almost identical radii of Al (1.25 Å), Ga (1.26 Å), together with the relatively similar substitution levels, one can see that the additivity of covalent-based radii is suggestive of subtle electronic effects at play. Similar phenomenology was observed for other structures of Al-bearing Zintl pnictides or tetrel-based compounds that usually have larger unit cell volumes than their isostructural Ga-analogs.

Table 4. Refined compositions, corresponding unit cell parameters, and occupancies on Sn 24k and 6c positions in the series of the binary type-I clathrates $A_8Sn_{46-x}\square_x$ ($A = Rb, Cs; x \approx 2$)¹.

Formula	<i>a</i> (Å)	Sn1A/Sn1B (24k)	Sn3 (6c)
$Rb_8Sn_{43.3(1)}$	12.0338(4)	0.770(3)/0.230	0.550(3)
$Rb_8Sn_{44.0(1)}$	12.0493(4)	0.681(2)/0.319	0.663(4)
$Cs_8Sn_{44.0(1)}$	12.0898(18)	0.680(4)/0.320	0.663(5)
$Cs_8Sn_{44.5(1)}$	12.1357(10)	0.831(11)/0.169	0.743(7)

¹ The corresponding CIFs have been deposited and have deposition numbers CSD 1989529–1989532.

A closer look at the data shows structural differences that are not apparent at first sight (Figure 2). Simply put, the $Cs_8Ga_8Sn_{38}$ structure is best modeled when the 24k site is split, while in the structure of the Rb-analog, the introduction of additional disorder appears to be unwarranted. During the refinement process, despite the convergence and low conventional *R*-values, a residual electron density peak of 3.6 e[−]/Å³ and a hole of −2 e[−]/Å³ near the Sn1 atom (24k site) were consistently observed. The situations seemed akin to what was also observed in the structure of binary Cs_8Sn_{44} (Table 4), where the missing framework atoms are believed to contribute to local distortions. After a case for additional positional disorder was established, refinements with splitting the 24k site into two positions with freed occupancies were attempted. These efforts helped us realize that the sum of occupancies of these two positions was close to 95%, indicating that one or both of them were mixed with a lighter Ga atom or holes. For a reference point, we draw attention to the fact that the s.o.f. of 24k site assigned as Sn also takes the approximate same value. Since it is not possible to model both split atoms being occupied by Sn and Ga simultaneously, one split 24k site, which corresponds to the Sn1B site in the

parent $\text{Cs}_8\text{Sn}_{44}$ structure, was set as Ga, whereas the site with the higher occupancy (Sn1A) was set as Sn (Figure 2b). Refined occupancies for Sn1 and Ga1 site (Table 2) were very close to that in the model without positional disorder but with only substitutional disorder on the single 24k site. Sn/Ga and Sn/Al ratios at the 24k site in $\text{Rb}_8\text{Ga}_8\text{Sn}_{38}$ (Table 2) and series $A_8\text{Al}_x\text{Sn}_{46-x}$ ($A = \text{K}, \text{Rb}; x \approx 8$), respectively, are also very similar to the reported value.

Having just mentioned the modeling of the 24k site disorder in $\text{Cs}_8\text{Ga}_x\text{Sn}_{46-x}$ and how it compares to other structures, $A_8\text{Al}_x\text{Sn}_{46-x}$ ($A = \text{K}, \text{Rb}; x \approx 8$) in particular, we must revisit the interpretation of some of our own work. To this end, we call attention to one of the published data files, where the presence of the small residual peak (ca. $2\text{e}^-/\text{\AA}^3$) near Sn1 atom can be seen [17]. It was previously believed to be an artifact of inadequate absorption correction, due to the single occurrence of such residual density within the realm of five other datasets that did not show this. Applying the above-described model to the abovementioned $\text{K}_8\text{Al}_x\text{Sn}_{46-x}$, we achieved an improvement in the *R*-values and reducing the largest residual electron density peak to $0.5\text{e}^-/\text{\AA}^3$. From this, we may conclude that the disorder-behavior in the ternary *A*-*Tr*-Sn system is also very complex, and that crystals from different reactions batches may exhibit both positional and substitutional disorder on Sn1 24k site. This issue, as discussed already, may prove to be critical in future works on the physical properties of these clathrates, and therefore, the structure must always be properly evaluated in order for the structure-property relationships to be understood.

The conformity just drawn between the disorder in $\text{Cs}_8\text{Ga}_x\text{Sn}_{46-x}$ and in the previously considered $\text{K}_8\text{Al}_x\text{Sn}_{46-x}$ is a validation of the applied model; however, we are cognizant of the fact that there remain uncertainties. Specifically, these are related to the possibility of a small number of vacancies presented at all framework sites since compositionally $\text{Cs}_8\text{Ga}_x\text{Sn}_{46-x}$ and $\text{Cs}_8\text{Ga}_x\text{Sn}_{46-x-y}\square_y$ for very low values of “*y*” cannot be distinguished. Another drawback of the model is the existence of the relatively short Ga1–Sn3/Ga3 contacts (Table 3, Figure 2b). The distance of $2.28\text{\AA}$ is shorter than any physical Ga–Sn, or even Ga–Ga contact; however, with the very low refined occupancies of ca. 12% and 36% on Ga1 and Ga3, respectively, this “averaged” short distance can certainly be avoided. One can envision a scenario in which there is some local ordering that does not follow the global symmetry rules.

Independent refinement of the occupancies on the remaining sites (16i and 6c sites), assigned as Sn atoms, confirmed them to be partially occupied, as expected. There were no problems with the difference Fourier map near these sites. This allowed us to model both 16i and 6c sites as mixed-occupied with Sn/Ga. Coordinates and displacement parameters were set to be equal and the total site occupancy was constrained to full.

Aside from the abovementioned difference concerning the 24k framework site, the remainder of the structural parameters follows the same general patterns. The site-occupation Ga/Sn preferences on the framework sites are similar to those seen in other type-I clathrates, with a clear tendency for the Ga atoms to occupy the 6c site (to avoid homoatomic Ga–Ga bonding) [3]. Refined occupancies in the Cs-bearing structure are very close to the earlier published isostructural compounds, $A_8\text{Al}_8\text{Sn}_{38}$ ($A = \text{K}, \text{Rb}$) and several others clathrates [3,17], whereas the Sn3 position in the Rb-bearing sample is occupied by Sn and Ga almost equally (Table 2). The 24k and 16i sites are mostly occupied by Sn atoms (ca. 85–95%).

Lastly, a brief comparison of the herein discussed $A_8\text{Ga}_x\text{Sn}_{46-x}$ ($A = \text{Rb}, \text{Cs}; x \approx 8$) structure and those of found in the literature is in order. Structural data for type-I clathrates $\text{Rb}_8\text{Ga}_8\text{Sn}_{38}$ and $\text{Cs}_8\text{Ga}_8\text{Sn}_{38}$ have been reported more than two decades ago; however, for inexplicable reasons, they are not retrievable from the ICSD database [30,31]. Another published work on the structural characterization of $A_8\text{Ga}_8\text{Sn}_{38}$ is also absent from the ICSD database, although the crystallographic analyses in the prior publications are from single-crystal XRD work and appear to be done with care [23,47]. Direct correlations between our data and the literature is hampered because of the nearly 100 K difference in the data-collections; however, assuming a typical value for the linear expansion coefficient ($\alpha \approx 10^{-5}\text{K}^{-1}$), one can see that the unit cell parameter for $\text{Cs}_8\text{Ga}_8\text{Sn}_{38}$ ($12.0792\text{\AA}$) [47] is

significantly higher than the room-temperature adjusted value (ca. 12.035 Å) for the currently considered $\text{Cs}_8\text{Ga}_{7.5(1)}\text{Sn}_{38.5}$. The other published data are also based on room temperature measurements, and the values for unit cell parameters of $\text{Rb}_8\text{Ga}_x\text{Sn}_{46-x}$ ($x = 8.17(60)$) and $\text{Cs}_8\text{Ga}_x\text{Sn}_{46-x}$ ($x = 7.90(14)$) are $a = 11.964(2)$ Å and $a = 12.006(2)$ Å, respectively [30,31]. These values are much closer to the results presented here, and correlate well with the slightly higher amount of Ga in the literature data. Neither of the three prior publications discuss the possibility for additional disorder by splitting the 24k site. One can also notice that in all cases the chemical formulae slightly deviate from the ideal Zintl count. The observed scatter in chemical compositions and structural difference for all known Sn-clathrates suggests that direct fusion of the elements in the sealed Nb-tubes does not allow precise compositional control.

In the last two paragraphs of this paper, we turn our attention to the binary type-I clathrates $\text{A}_8\text{Sn}_{44}\square_2$ ($A = \text{Rb}, \text{Cs}$), which have been studied previously [34,35,48]. The brief recap on the positional and occupational disorder in these two structures is instructive within the context of this study, as the discovery in $\text{Cs}_8\text{Sn}_{44}\square_2$ suggested a model for the disorder in $\text{Cs}_8\text{Ga}_8\text{Sn}_{38}$. Furthermore, we speculated that the final structure/composition of the clathrates with Ga/Sn mixed occupied framework are highly dependent on the experimental conditions, which could also be applicable to binaries.

An interesting point is related to the formation of binary $\text{A}_8\text{Sn}_{44}\square_2$ ($A = \text{Rb}, \text{Cs}$) phases, which can be regarded as Zintl phases. The charge balance in such compounds can be achieved by the presence of the defects in the framework [34,47,48]. Typically, deficiency is achieved by the vacancy at 6c Sn site, making this position partially occupied with the s.o.f. of ca. 0.66. At room temperature, the $\alpha\text{-A}_8\text{Sn}_{44}\square_2$ phase adopts the type-I clathrate structure with a $2 \times 2 \times 2$ superstructure ($Ia\bar{3}d$ space group) of the primitive cubic unit cell ($Pm\bar{3}n$), which originates from a partial ordering of defects. The reversible transformation into the high-temperature β -form with the smaller unit cell with primitive symmetry occurs at the temperatures higher than 330 K [35,45,48–50]. However, our SCXRD experiments performed at 200(2) K showed that some datasets could be indexed in $Pm\bar{3}n$ space group (Table 4), whereas other datasets show super-structure reflections consistent with the $Ia\bar{3}d$ model. One of the possible explanations for such an observation is the vacancies are also locally ordered, just like the speculated local ordering of Ga atoms in $\text{A}_8\text{Ga}_x\text{Sn}_{46-x}$ ($A = \text{Rb}, \text{Cs}; x \approx 8$), vide supra. Therefore, depending on either synthetic conditions or quality of the single crystals, the diffraction could paint a different picture for the “same” sample. The unit cell parameters from single-crystal X-ray diffraction presented in Table 4 can be considered indirect evidence for the above conjecture. These data do not affect the main discussion but rather helps with the comparison of unit cell parameters for binary and ternary clathrates.

The refined unit cell parameters, obtained from SCXRD work, together with the refined structures demonstrate some compositional deviations from the ideal 8:44 ratio (Table 4). Since a split Sn1 site (24k) in $\text{A}_8\text{Sn}_{44}\square_2$ is also present, the ca. 66% partially occupied Sn3 (6c) site can be considered the reason for the displacement of Sn1 from its ideal position—some published datasets display clear correlation between the s.o.f. for the Sn1 split sites and the s.o.f. of the Sn3 site [35,49]. This scenario perfectly describes a hypothetical ordered model, especially if the splitting ratio is exactly 2:1, matching the number of filled and vacant Sn3 atoms. This is the case with $\text{Rb}_8\text{Sn}_{44.0(1)}$ and $\text{Cs}_8\text{Sn}_{44.0(1)}$ (Table 4). Indeed, as can be seen in Figure 2b, a simultaneous occupation of Sn1A (24k) and Sn3 (6c) sites in binary compounds is favorable due to the reasonable bond distance values. However, it is a rather conspicuous case, which is not always applicable. As seen from Table 4, small variations in the Sn content can be correlated with s.o.f. on the Sn3 (6c) site and unit cell volumes. An observed trend is quite straightforward, with fewer vacancies in conjunction with a larger unit cell. Occupancy of Sn3 (6c) site is always smaller than s.o.f. for Sn1A (24k) site, due to the impossibility of the simultaneous existence of Sn1B and Sn3 positions and therefore short Sn1B–Sn3 contact (Figure 2b).

4. Conclusions

Single crystals of type-I clathrates $\text{Rb}_8\text{Ga}_{7.1(1)}\text{Sn}_{38.9}$ and $\text{Cs}_8\text{Ga}_{7.5(1)}\text{Sn}_{38.5}$ were synthesized via a conventional high-temperature method in sealed niobium tubes. The cubic crystal structures were confirmed by single-crystal X-ray diffraction. Both clathrates show substitution of Sn by Ga atoms at all three atomic sites 6c, 16i, and 24k. The Cs-bearing clathrate demonstrates the first example of a complex combined substitutional and positional disorder in ternary clathrates, which can be considered a superposition between the structure of undoped $\text{Cs}_8\text{Sn}_{44}\square_2$ and idealized positional-disorder-free $\text{A}_8\text{Ga}_8\text{Sn}_{38}$. Considering the electron count, all reported clathrates can be regarded as nearly charge-balanced Zintl phases which are likely to exhibit heavily doped semiconducting behavior.

We speculate that such highly disordered crystals should demonstrate enhanced thermoelectric performance compared to the less-disordered ones, due to the lowering of the thermal conductivity. This reasoning remains to be confirmed experimentally after development of the target synthesis of such phases.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/10/4/298/s1>, Figure S1: Room temperature powder X-ray diffraction pattern of representative polycrystalline $\text{A}_8\text{Ga}_x\text{Sn}_{46-x}$ ($\text{A} = \text{Rb}, \text{Cs}$; $x \approx 8$) phase. All discussed samples are similar. Calculated pattern is simulated from the crystallographic data of Cs-bearing phase presented in Table 1. β -Sn phase marked with an asterisk (*).

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