Synthesis and Structural Characterization of the New Clathrates $K_8Cd_4Ge_{42}$, $Rb_8Cd_4Ge_{42}$, and $Cs_8Cd_4Ge_{42}$

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Abstract: This paper presents results from our exploratory work in the systems K-Cd-Ge, Rb-Cd-Ge, and Cs-Cd-Ge, which yielded the novel type-I clathrates with refined compositions $K_{8.77(7)}Cd_{3.77(7)}Ge_{42.23}$, $Rb_{8.65(7)}Cd_{3.65(7)}Ge_{42.35}$, and $Cs_{7.80(1)}Cd_{3.65(6)}Ge_{42.35}$. The three compounds represent rare examples of clathrates of germanium with the alkali metals, where a $d^{10}$ element substitutes a group 14 element. The three structures, established by single-crystal X-ray diffraction, indicate that the framework-building Ge atoms are randomly substituted by Cd atoms on only one of the three possible crystallographic sites. This and several other details of the crystal chemistry are elaborated.

Keywords: clathrates; type-I structure; germanium; cadmium; Zintl phases

1. Introduction

Clathrates of silicon and germanium with the alkali metals have been known now for almost half a century [1]. The idea of phonon-glass electron-crystal (PGEC), coined by G. Slack [2], succinctly captures the two most important structural features of these clathrates: rigid open frameworks, made up of covalently bonded atoms, and guest atoms residing in the large cages. The stable frameworks contribute to the favorable carrier mobilities, while the filler atoms that vibrate (or “rattle”, as is frequently said) in the oversized cages are believed to be the reason for the low lattice thermal conductivity exhibited by many clathrates. Therefore, this class of compounds has gained interest for their prospects as thermoelectric materials [2–5].

Most studied clathrate compounds are based on the group 14 elements Si, Ge, and Sn ($T_1$). These atoms form extended networks adopting several different structure types. Fractions of the framework atoms can be substituted by group 13 and 12 elements, as well as late transition metals ($M$), which can be stabilized in tetrahedral coordination. There are large cages in the clathrate structures, which are partially or fully occupied by guest atoms ($A$). The typical guest atoms are alkali metals, alkaline earth metals, or Ce and Eu from the rare earth metals [6–10].

This paper deals with three new clathrate phases with compositions $K_{8.77(7)}Cd_{3.77(7)}Ge_{42.23}$, $Rb_{8.65(7)}Cd_{3.65(7)}Ge_{42.35}$, and $Cs_{7.80(1)}Cd_{3.65(6)}Ge_{42.35}$, which adopt the type-I structure (Figure 1). The nominal formula for this structure is $A_8(Cd,Ge)_{46}$, and it boasts cages of 20- and 24-atoms. Here, we would like to mention that numerous clathrates of germanium with the alkali metals are known as of today, but this study is among very few to identify cadmium as a substituent of germanium-based clathrates—the quaternary phase $K_4Eu_2Cd_3Ge_{41}$ appears to be the only report of similar chemistry so far [11]. The corresponding systems K-M-Ge and Rb-M-Ge with $M$ being the group 12 elements Zn and Hg have already been explored, and the structures of the type-I clathrates $K_8Zn_4Ge_{42}$ [12], $K_8Hg_{63.19}Ge_{42.81}$, and $Rb_8Hg_{63.03}Ge_{42.97}$ [13] have been published.
2. Results

2.1. Crystallographic Analysis

The structure solutions and refinements proceeded in a straightforward manner (Table 1), and only a few details deserve special mention. First, the contrast between the X-ray atomic scattering factors of Cd and Ge is significant, allowing precise refinements of the site occupation factors should there be mixed-occupied sites. Indeed, in all cases, when the occupancies of the framework sites were first freely refined (individually, while the remaining ones were kept fixed), it was noted that the occupation factors for 16i and 24k sites did not deviate from 100%, while sites 6c in all three structures appeared to be “heavier”. This indicates that Cd (Z = 48) and Ge (Z = 32) co-occupy framework site 6c only (in a ratio ca. 60% Cd, 40% Ge). Such distribution of group 12 and group 14 elements is consistent with the published refinements for K₈H₃₃.₃₉Ge₄₂.₈₁ and Rb₈H₃₃.₃₉Ge₄₂.₉₇ [13], K₆Zn₃.₄₆Si₄₂.₅₄ and Rb₇.₆₆Zn₃.₆₅Si₄₂.₃₇ [14], and K₆Zn₃.₇₈Sn₄₂.₂₂, Rb₂Zn₃.₃₂Sn₄₂.₄₈, and Cs₈Zn₃.₄₄Sn₄₂.₅₆ [15]. If one considers the alkaline earth clathrates, such as Ba₈Zn₇Si₃₉ [16], the 6c site is also mostly occupied by Zn (77% Zn, 23% Si), with the remainder of the Zn found at 24k (9% Zn, 91% Si).

Notice that, in all three structures, the Zintl-Klemm concept [17], which appears to be followed by many other clathrates [8], is not completely satisfied by the above-mentioned compounds. For instance, based on the rationalization \([A^+]_₉[Me^{2-}]_₄[TL^{10}]_{42}\), one should expect the structural formulae to be \(A₈M₄TL₄₂\) (\(A\) = alkali metal, \(M\) = Zn, Cd, Hg; \(T\) = tetrel, or Si, Ge, Sn). The same holds true for \(Ba₈Zn₈Si₃₈\) (=\([Ba^+]₉[Zn^{2-}]_₈[Si^{10}]_{3₈}\)). The reasons for the slightly lower refined content of Zn, Cd, or Hg are not yet understood. This would mean, however, that all these materials are metallic conductors, not semiconductors, as expected from the Zintl-Klemm concept. One might argue that the structures have both Cd/Ge positional disorder and defects on the 6c sites, i.e., in analogy with Ba₈Zn₇Ge₄₆–₃–y\(\square\)_y and Ba₈Cd₄Ge₄₆–₃–y\(\square\)_y (\(\square\) = vacancy) [18,19]. This certainly is a valid argument, which warrants further investigations. We will note here that, while for Ba₈Zn₇Ge₄₆–₃–y\(\square\)_y and Ba₈Cd₄Ge₄₆–₃–y\(\square\)_y the hypothesis for vacancies in the framework had been supported by the low occupation factors and elongated displacement parameters of the atoms neighboring the defects, none of these indicators of additional structural disorder are observed for the herein discussed structures.

Figure 1. Schematic view of the clathrate with type-I structure. For the drawing, the structural information for Cs₇.₈₀₁(Cd₃.₆₅₆)₆Ge₄₂.₃₅ was used and the atoms are labeled accordingly.
This is the center of the smaller pentagonal dodecahedral cage in the type-I clathrate, which might be position is not fully occupied. Indeed, when the occupation factor of Cs₂ is freed, the difference Fourier map flattens out completely (Tables 1 and 2).

We also need to mention the fact that when checking the occupancies of the guest atoms in the reported structures 1 and 2, they did not deviate from full. However, when the occupancies of the Cs sites in 3 were checked, it became obvious that site 2a is underoccupied (occupation factor 89.8(4)%). This is the center of the smaller pentagonal dodecahedral cage in the type-I clathrate, which might be not large enough to accommodate the very large Cs atom. Therefore, 3 is the only structure without 100% filled cages, refined as Cs₇(80(1))Cd₃(65(6))Ge₄₂(23). To help the reader of this article appreciate the subtleties of the refinements Cs₇(80(1))Cd₃(65(6))Ge₄₂(23) vs. Cs₈Cd₃(65(6))Ge₄₂(23), the .CIF for the latter is provided as supporting evidence (please see the supplementary electronic information associated with this article). Despite the respectable residuals, quick convergence and quite reasonable anisotropic displacement parameters, the relatively deep hole in the difference electron density map (the Fourier synthesis indicates a hole of 4 e⁻/Å³ just 0.2 Å away from Cs2) is a telling sign that the respective position is not fully occupied. Indeed, when the occupation factor of Cs2 is freed, the difference Fourier map flattens out completely (Tables 1 and 2).

Table 1. Selected crystal data and structure refinement parameters for K₈Cd₃(77(7))Ge₄₂(23) (1), Rb₈Cd₃(65(6))Ge₄₂(23) (2), and Cs₇(80(1))Cd₃(65(6))Ge₄₂(23) (3).

| Compound | 1 | 2 | 3 |
|----------|---|---|---|
| Fw/g mol⁻¹ | 3803.2 | 4170.2 | 4519.1 |
| Crystal system | Cubic | Cubic | Cubic |
| Space group | Pm 3n (No. 223), Z = 1 | Pm 3n (No. 223), Z = 1 | Pm 3n (No. 223), Z = 1 |
| a/Å | 10.8710(4) | 10.9099(5) | 10.9643(7) |
| V/Å³ | 1284.72(8) | 1298.56(10) | 1318.08(15) |
| T/K | 200(2) | | |
| Radiation | Mo Kα, λ = 0.71073 Å | | |
| ρ/ρ cm⁻³ | 4.92 | 5.33 | 5.69 |
| μ/cm⁻¹ | 264.3 | 329.7 | 304.7 |
| data/restraints/parameters | 291/0/17 | 318/0/17 | 327/0/18 |
| R₁ (I > 2σ(I)) a | 0.0182 | 0.0178 | 0.0138 |
| wR₂ (I > 2σ(I)) a | 0.0359 | 0.0365 | 0.0298 |
| R₁ (all data) a | 0.0241 | 0.0323 | 0.0180 |
| wR₂ (all data) a | 0.0378 | 0.0836 | 0.0314 |
| GOF | 1.156 | 1.064 | 1.116 |
| largest peak & hole/e⁻. Å⁻³ | 0.54 & -0.57 | 0.62 & -0.85 | 0.63 & -0.56 |

*a R₁ = \|F₁| - |Fο|/\|Fο\|, wR₂ = [(\|w(Fο²/F₁²)\|²)/∑w(Fο²/F₁²)]^{1/2}, where w = 1/|σ²Fο² + (A - P)^2 + (B - P)|, and P = (Ea² + 2Eb²)/3, A and B weight coefficients.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Ueq/Å²) for K₈Cd₃(77(7))Ge₄₂(23) (1), Rb₈Cd₃(65(6))Ge₄₂(23) (2), and Cs₇(80(1))Cd₃(65(6))Ge₄₂(23) (3).

| Atom | Site | x/a | y/b | z/c | Occupancy | Ueq a |
|------|------|-----|-----|-----|-----------|-------|
| K1  | 6d   | 0   | 1/4 | 1/2 | 100%      | 0.0358(7) |
| K2  | 2a   | 0   | 0   | 0   | 100%      | 0.0175(9) |
| Ge1 | 24k  | 0   | 0.30355(5) | 0.11589(5) | 100% | 0.0129(2) |
| Ge2 | 16i  | 0.18327(4) | x | x | 100% | 0.0119(2) |
| Ge/Cd3 | 6c | 1/4 | 0 | 1/2 | 37(1)/63(1)% | 0.0137(3) |

| Rb1 | 6d   | 0    | 1/4 | 1/2 | 100% | 0.0254(3) |
| Rb2 | 2a   | 0    | 0   | 0   | 100% | 0.0124(3) |
| Ge1 | 24k  | 0    | 0.30365(5) | 0.11637(5) | 100% | 0.0123(2) |
| Ge2 | 16i  | 0.18356(3) | x | x | 100% | 0.0114(2) |
| Ge/Cd3 | 6c | 1/4 | 0 | 1/2 | 39(1)/61(1)% | 0.0127(3) |
Lastly, while commenting on the size of the guest atoms and the clathrate cages, we should point the attention to the anisotropic displacement parameter of K1 in structure 1, site 6d (Table 3). This atom is at the center of the larger tetrakaidecahedral cage (Figure 2). The size/shape of the thermal ellipsoid is not dependent on the site occupation factor (deviates from unity less than 3\(\sigma\)). The equivalent isotropic displacement parameter for K1 is, by far, the largest of all. Its slightly oblate shape may hint at off-centering (Table 3), but such positional disorder is very small and could not be resolved from the available crystallographic data. For comparison, the disorder in the type-I clathrates of tin, where the tetrakaidecahedral cages are even larger, is easily modeled from data collected on an in-house diffractometer [20–22]. Sr\(_8\)Ga\(_{16}\)Ge\(_{30}\) and Ba\(_8\)Ga\(_{16}\)Ge\(_{30}\) are other well-known examples of filler atoms being off-centered from their equilibrium positions, and both structures have been worked out from synchrotron and neutron diffraction data [23–25].

Table 3. Anisotropic displacement parameters (U\(_{ij}\) / Å\(^2\)) for K\(_8\)Cd\(_{3.77(7)}\)Ge\(_{42.23}\) (1), Rb\(_8\)Cd\(_{3.65(7)}\)Ge\(_{42.35}\) (2), and Cs\(_{7.80(1)}\)Cd\(_{3.65(6)}\)Ge\(_{42.35}\) (3).

| Atom   | Site |  x/a |  y/b |  z/c | Occupancy  | U\(_{eq}\) \(^a\) |
|--------|------|------|------|------|------------|---------------|
| Cs1    | 6d   |  0   |  1/4 |  1/2 | 100%       | 0.0204(2)     |
| Cs2    | 2a   |  0   |  0   |  0   | 89.8(4)%   | 0.0117(3)     |
| Ge1    | 24k  |  0   |  0.30334(4) | 0.11719(4) | 100%       | 0.0123(1)     |
| Ge2    | 16i  | 0.18370(3) | x   | x   | 100%       | 0.0116(2)     |
| Ge/Cd3 | 6c   |  1/4 |  0   |  1/2 | 39(1)/61(1)% | 0.0136(3)     |

\(^a\) U\(_{eq}\) is defined as one third of the trace of the orthogonalized U\(_{ij}\) tensor.
and the corresponding distances (see Table 4), which fall in the intervals of vide supra. K is slightly smaller than that of Cd (8 Å), but the refined Hg content in K²Cd₃Ge₄₄ is 10.8238(2) Å, respectively. Of course, the presence of vacancies in the framework for K²Hg₃Ge₄₄ should not be overlooked, as it contributes to the contraction of the unit cell. Given that Cd and In are neighboring elements in the periodic chart with similar atomic sizes, this can be also observed in Table 1, the unit cell parameters of the three cubic type-I clathrates (space group Pm 3n (No. 223)) increase from a = 10.8710(4) Å for K²Cd₃Ge₄₄ to a = 10.9099(5) Å for Rb₂Cd₃Ge₄₄. This increase can be attributed to the increase in size of the alkali metal atoms (rₓ ≈ 2.03 Å; rₚ = 2.16 Å, respectively). Of course, the presence of vacancies in the framework for K²Ge₄₄ and Cs₈Ge₄₄ (□ = vacancy) should not be overlooked, as it contributes to the contraction of the unit cell. Given that Cd and In are neighboring elements in the periodic chart with similar atomic radii (rᵢn ≈ 1.42 Å), it is no surprise that the type-I clathrates from the systems K-In-Ge, Rb-In-Ge, and Cs-In-Ge show similar characteristics. The unit cell parameters of the latter increase are in the following order: a = 10.997(2) Å for K₈In₈Ge₄₄; a = 11.033(2) Å for Rb₈In₇Ge₃₈; a = 11.079(2) Å for Cs₈In₈Ge₃₈. Another relevant comparison can be made between K²Cd₃Ge₄₄ and Cs₈Zn₄Ge₄₂ on the one hand, and K₈Zn₄Ge₄₂ and K₈Hg₃Ge₄₂ on the other [12,13]. The atomic size of Zn is slightly smaller than that of Cd (rₓZn ≈ 1.21 Å), hence the unit cell parameter for K₈Zn₄Ge₄₂ (a = 10.7488(1) Å) [12]. Mercury and cadmium are very similar in size (rₓCd ≈ 1.38 Å; rₓHg ≈ 1.39 Å), but the refined Hg content in K₈Hg₃Ge₄₂ is lower than the Cd content in K²Cd₃Ge₄₂, hence the smaller unit cell parameter for the former (a = 10.8489(13) Å) [13]. The same is true for Rb₂Cd₃Ge₄₂ (a = 10.8750(13) Å) [13].

The net result of the substitution of the larger Cd for the smaller Ge is a small increase in the cage sizes, and therefore an expansion of the unit cells (vide supra). This can be also observed in the atomic distances (see Table 4), which fall in the intervals of dₓGe-Ge = 2.4931(4) to 2.52(1) Å for 1, dₓGe-Ge = 2.5029(4) to 2.539(1) Å for 2, and dₓGe-Ge = 2.5118(4) to 2.570(1) Å for 3, respectively. Notice that, since Cd substitutes only at the 6c site, Cd-Cd contacts are avoided. This site only neighbors Ge1 and the corresponding dₓCd/Ge3-Ga1 distances monotonically increase in the following order: 2.5858(6) Å.
for 1, 2.5912(5) Å for 2, and 2.6019(5) Å for 3, respectively. The distances from the guest atoms in the cages to the framework follow the same trend (Table 4).

Table 4. Selected interatomic distances for K\textsubscript{8}Cd\textsubscript{3.77(7)}Ge\textsubscript{42.23} (1), Rb\textsubscript{8}Cd\textsubscript{3.65(7)}Ge\textsubscript{42.35} (2), and Cs\textsubscript{7.80(1)}Cd\textsubscript{3.65(6)}Ge\textsubscript{42.35} (3).

| Compound 1       | d Å | Compound 2       | d Å | Compound 3       | d Å |
|------------------|-----|------------------|-----|------------------|-----|
| Ge1-Ge2 (2 ×)    | 2.4931(4) | Ge1-Ge2 (2 ×)    | 2.5029(4) | Ge1-Ge2 (2 ×)    | 2.5118(4) |
| Ge1-Ge1          | 2.520(1)  | Ge1-Ge1          | 2.539(1)  | Ge1-Ge1          | 2.570(1)  |
| Ge1-Ge/Cd3       | 2.5858(6) | Ge1-Ge/Cd3       | 2.5912(5) | Ge1-Ge/Cd3       | 2.6019(5) |
| Ge2-Ge2          | 2.513(1)  | Ge2-Ge2          | 2.511(1)  | Ge2-Ge2          | 2.518(1)  |
| Ge2-Ge1 (3 ×)    | 2.4931(4) | Ge2-Ge1 (3 ×)    | 2.5029(4) | Ge2-Ge1 (3 ×)    | 2.5118(4) |
| Ge/Cd3-Ge1 (4 ×) | 2.5858(6) | Ge/Cd3-Ge1 (4 ×) | 2.5912(5) | Ge/Cd3-Ge1 (4 ×) | 2.6019(5) |
| K1-Ge1 (8 ×)     | 3.6789(4) | Rb1-Ge1 (8 ×)    | 3.6932(4) | Cs1-Ge1 (8 ×)    | 3.7167(4) |
| K1-Ge2 (8 ×)     | 4.0438(3) | Rb1-Ge2 (8 ×)    | 4.0564(3) | Cs1-Ge2 (8 ×)    | 4.0758(3) |
| K1-Ge/Cd3 (4 ×)  | 3.8435(2) | Rb1-Ge/Cd3 (4 ×) | 3.8572(2) | Cs1-Ge/Cd3 (4 ×) | 3.8765(2) |
| K1-Ge1 (4 ×)     | 4.2157(6) | Rb1-Ge1 (4 ×)    | 4.2262(5) | Cs1-Ge1 (4 ×)    | 4.2378(5) |
| K2-Ge2 (8 ×)     | 3.4507(7) | Rb2-Ge2 (8 ×)    | 3.4686(6) | Cs2-Ge2 (8 ×)    | 3.4885(6) |
| K2-Ge1 (12 ×)    | 3.5322(6) | Rb2-Ge1 (12 ×)   | 3.5477(5) | Cs2-Ge1 (12 ×)   | 3.5654(5) |

### 3. Discussion

In 2014, we reported for the very first time the occurrence of the type-I and type-II clathrates Rb\textsubscript{3.20}Na\textsubscript{2.80}[Zn\textsubscript{3.85}Si\textsubscript{42.15}] and Rb\textsubscript{8}Na\textsubscript{16}Zn\textsubscript{8}Si\textsubscript{127.61} [31]. Shortly after, another team reported the structure determination for K\textsubscript{8}Zn\textsubscript{3.46}Si\textsubscript{42.54} and Rb\textsubscript{7.86}Zn\textsubscript{3.63}Si\textsubscript{42.37} [14]. Subsequently, we set out to synthesize the Cd-analogs of these compounds, but these studies did not yield any clathrates.

As a result, we turned our attention to the germanium clathrates. We noticed that there were prior reports on K\textsubscript{8}Zn\textsubscript{4}Ge\textsubscript{42} and the mixed-cation K\textsubscript{8}Ba\textsubscript{8–x}Zn\textsubscript{x}Ge\textsubscript{46–y} [12]. K\textsubscript{8}H\textsubscript{3.19}Ge\textsubscript{42.81} and Rb\textsubscript{8}H\textsubscript{3.03}Ge\textsubscript{42.97} [13] have also been known for some time. The mixed-cation clathrates K\textsubscript{8}E\textsubscript{12}Zn or Cd\textsubscript{12}Ge\textsubscript{41} also appear in the literature [11], but the corresponding crystallographic information is not available from the ICSD.

Given that mercury and cadmium are very similar in size, we thought it was surprising that the corresponding K-Cd-Ge, Rb-Cd-Ge, and Cs-Cd-Ge systems had not been carefully explored. This work fills this gap in the literature by detailing the structures of the type-I clathrates K\textsubscript{8}Cd\textsubscript{3.77(7)}Ge\textsubscript{42.23}, Rb\textsubscript{8}Cd\textsubscript{3.65(7)}Ge\textsubscript{42.35}, and Cs\textsubscript{7.80(1)}Cd\textsubscript{3.65(6)}Ge\textsubscript{42.35}. However, the latter clathrate phases are always co-crystallizing with small amounts of secondary phases, irrespective of the tried different synthesis routes. As mechanical separation was not achievable either, measurements of the transport properties could not be performed.

In further investigations, we will aim to resolve the synthetic problems leading to impurity phases and study the transport properties. One of our more distant goals will be to explore the systems Cs-Na-Cd-Ge and Rb-Na-Cd-Ge. The mixed cations (large and small) can prove promising for synthesizing the hitherto unknown Cs\textsubscript{8}Na\textsubscript{16}Cd\textsubscript{12}Ge\textsubscript{124} and Rb\textsubscript{8}Na\textsubscript{16}Cd\textsubscript{12}Ge\textsubscript{124} type-II clathrates. We will recall that the crystal chemistry and the chemical bonding in many type-I clathrate structures are satisfactorily understood because they are more easily accessible in ternary systems. For type-II clathrates, the difficulty of synthesizing selectively new compounds remains an open challenge, which has been attributed to the fact that the cavities of the type-II clathrates have a larger difference in size. Therefore, we have speculated (and have shown experimentally on the examples of (Cs or Rb)\textsubscript{8}Na\textsubscript{16}(Si or Ge)\textsubscript{136} [32]) that the directed synthesis of type-II can be greatly facilitated by choosing spatially different guest atoms. This idea, combined with the proper choice of a framework-substituent, can lead to new clathrate type-II, as demonstrated by the subsequent studies on Cs\textsubscript{8}Na\textsubscript{16}Ag\textsubscript{8–y}Ge\textsubscript{129.3} [33] and Cs\textsubscript{8}Na\textsubscript{16}Cu\textsubscript{8}Ge\textsubscript{131} [34]. Very recently, the applicability of notion that two types of different guest atoms will be preferred for the complete and ordered filling of both cavities in the type-II compounds was confirmed for the tin-based Cs\textsubscript{8}Ba\textsubscript{16}Ga\textsubscript{39.5}Sn\textsubscript{96.3} and...
suggesting that the Cs-Ba-Cd-Ge and Rb-Ba-Cd-Ge systems are worthy candidates for further investigations.

4. Materials and Methods

4.1. Synthesis

The syntheses were carried out by loading stoichiometric mixtures of the respective elements in suitably prepared Nb tubes, which were then sealed by arc-welding.

Due to the extremely high reactivity of the alkali metals to moisture and oxygen, all manipulations were done with great care in an argon-filled glove box. The atmosphere in the glovebox was maintained at \( \text{O}_2/\text{H}_2\text{O} \) level below 1 ppm. The elements were purchased from Alfa or Sigma-Aldrich with a stated purity higher than 99.9 wt % (metal basis). In order to carry out the reactions in a safe and reliable manner, the elements were weighed in a ratio of \( A:M:Ge = 8:4:42 \) (\( A = \text{K, Rb, Cs} \)). Total mass in each case was ca. 300 mg. After arc-welding, the Nb tubes with the reactants inside were enclosed in fused silica tubes. Under dynamic vacuum, the fused silica tubes were baked and then flame-sealed.

The samples were heated slowly in programmable muffle furnaces to 950 °C with a rate of 10 °C/h, annealed for 15 h, and then cooled down (rate −150 °C/h) to 650 °C, dwelled for 4 d, and cooled down (rate −5 °C/h) to room temperature. The obtained type-I clathrates were stable in air and moisture and were handled on the bench. Based on the powder X-ray diffraction patterns, the yields were high, estimated to be over 70–80 wt %, with some small impurity phases, yet unidentified, present in each specimen.

4.2. Powder X-ray Diffraction

X-ray powder diffraction patterns of selected crystals were carried out at room temperature on a Rigaku MiniFlex powder diffractometer using Cu-K\( \alpha \) radiation. The data collection scans were done in \( \theta-\theta \) mode (\( 2\theta_{\text{max}} = 65^\circ \)) with a step of 0.05° and 2 s/step counting time. The data were analyzed with the JADE 6.5 software package. The intensities and the positions of the experimentally observed peaks and those calculated based on the corresponding single-crystal structures matched very well with one another.

4.3. Single-Crystal X-ray Diffraction

Single-crystal X-ray diffraction data were collected on a Bruker CCD-based diffractometer using graphite-monochromated Mo-K\( \alpha \) radiation (\( \lambda = 0.71073 \) Å). Temperature was maintained at 200(2) K. Suitable single-crystals from each compound were selected and cut to smaller dimensions (less than 0.1 mm) under mineral oil. The SMART [36] and SAINTplus [37] programs were used for the data collection, integration, and the global unit cell refinement from all data. Semi-empirical absorption correction based on equivalent reflections was applied with SADABS [38]. The structures were refined to convergence by full-matrix least-square methods on \( F^2 \), as implemented in SHELXTL [39]. All sites were refined with anisotropic displacement parameters.

Selected details of the data collections and structure refinement parameters are listed in Table 1. The atomic coordinates and equivalent isotropic displacement parameters are given in Table 2. The anisotropic displacement parameters are tabulated in Table 3, and selected interatomic distances are summarized in Table 4. Additional details of the crystal structure analyses may be requested from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Karlsruhe, Germany) on quoting the depository numbers CSD-430998 for \( \text{K}_8\text{Cd}_{3.77(7)}\text{Ge}_{42.23} \), CSD-430999 for \( \text{Rb}_8\text{Cd}_{3.65(7)}\text{Ge}_{42.35} \), and CSD-431000 for \( \text{Cs}_{7.80(1)}\text{Cd}_{3.65(6)}\text{Ge}_{42.35} \), respectively.

4.4. Energy-Dispersive Analysis

Multiple crystals for each composition were analyzed by means of energy dispersive X-ray spectroscopy (EDX). Data were gathered using a JEOL 7400F electron microscope equipped with an
INCA-OXFORD energy-dispersive spectrometer. Only the specified elements (i.e., no unrecognized impurities) could be detected in ratios consistent with the refined compositions.

5. Conclusions

With this paper, our team presented the synthesis and the structural characterization of the type-I clathrates $K_8Cd_{3.77(7)}Ge_{42.23}$, $Rb_8Cd_{3.65(7)}Ge_{42.35}$, and $Cs_7,800(Cd_{3.65(6)}Ge_{42.35})$. In the future, we will be exploring the systems $Cs$-$Na$-$Cd$-$Ge$ and $Rb$-$Na$-$Cd$-$Ge$. Based on the presented results and the overview of the current literature, we believe that using mixed cations (large and small) can yield the hitherto unknown $Cs_8Na_{16}Cd_{12}Ge_{124}$ and $Rb_8Na_{16}Cd_{12}Ge_{124}$ type-II clathrates.

Supplementary Materials: The following are available online at www.mdpi.com/1996-1944/9/4/236/s1. Structure refinement for $Cs_8Cd_{3.65(6)}Ge_{42.35}$, in .CIF.

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Author Contributions: Marion C. Schäfer and Svilin Bobev conceived and designed the experiments; Marion C. Schäfer performed the experiments; Marion C. Schäfer and Svilin Bobev analyzed the data; Svilin Bobev wrote the paper.

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Abbreviations

The following abbreviations are used in this manuscript:

| Abbreviation | Description                          |
|--------------|--------------------------------------|
| PGE C        | Phonon-Glass Electron-Crystal        |
| Tt           | Tetrle, group 14 elements Si, Ge and Sn |
| $A$          | group 1, 2 and 3 elements, which partially or fully occupy the cages within the clathrate framework |
| $M$          | group 13 and 12 elements, as well as late transition metals, substituting framework atoms |
| $\Box$       | vacancy                              |

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