Cage-Forming Compounds in the Ba–Rh–Ge System: From Thermoelectrics to Superconductivity

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ABSTRACT: Phase relations and solidification behavior in the Ge-rich part of the phase diagram have been determined in two isothermal sections at 700 and 750 °C and in a liquidus projection. A reaction scheme has been derived in the form of a Schulz–Scheil diagram. Phase equilibria are characterized by three ternary compounds: $\tau_1$-Ba$_3$Rh$_4$Ge$_{16}$ (BaNi$_5$In$_7$-type) and two novel phases, $\tau_2$-Ba$_3$Rh$_{15}$Ge$_{36}$ and $\tau_3$-Ba$_5$Rh$_{15}$Ge$_{36}$, both forming in peritectic reactions. The crystal structures of $\tau_2$ and $\tau_3$ have been elucidated from single-crystal X-ray intensity data and were found to crystallize in unique structure types: Ba$_3$Rh$_4$Ge$_{16}$ is tetragonal ($I4/mmm$, $a = 0.65643(2)$ nm, $c = 2.20367(8)$ nm, and $R_p = 0.0273$), whereas atoms in Ba$_3$Rh$_{15}$Ge$_{36}$ ($x = 0.25$) arrange in a large orthorhombic unit cell ($Fddd$, $a = 0.84570(2)$ nm, $b = 1.4725(2)$ nm, $c = 6.644(3)$ nm, and $R_p = 0.034$). The body-centered-cubic superstructure of binary Ba$_3$Ge$_4$ reveals a maximum solubility of $x = 1.2$ Rh atoms in the structure at a vacancy level of $y = 2.0$. The cubic lattice parameter increases with increasing Rh content. Clathrate I decomposes eutectoidally at 740 °C: $\kappa_1$-Ba$_4$Rh$_{16}$Ge$_{46}$+$\tau_2$, while the clathrate type I phase, $\kappa_1$-Ba$_4$Rh$_{16}$Ge$_{46}$+$\tau_2$, reveals a maximum solubility of $x = 1.2$ Rh atoms in the structure at a vacancy level of $y = 2.0$. The cubic lattice parameter increases with increasing Rh content. Clathrate I decomposes eutectoidally at 740 °C: $\kappa_1$-Ba$_4$Rh$_{16}$Ge$_{46}$+$\tau_2$. A very small solubility range is observed at 750 °C for the clathrate IX, $\kappa_4$-Ba$_5$Rh$_{15}$Ge$_{36}$+$\tau_3$ ($x \sim 0.16$). Density functional theory calculations have been performed to derive the enthalpies of formation and densities of states for various compositions Ba$_3$Rh$_{15}$Ge$_{36}$-$\tau_3$ ($x = 0.6$). The physical properties have been investigated for the phases $\tau_2$, $\tau_3$, and $\kappa_1$, documenting a change from thermoelectric ($\kappa_1$) to superconducting behavior ($\tau_2$). The electrical resistivity of $\kappa_1$-Ba$_4$Rh$_{16}$Ge$_{46}$ increases almost linearly with the temperature from room temperature to 730 K, and the Seebeck coefficient is negative throughout the same temperature range. $\tau_1$-Ba$_3$Rh$_4$Ge$_{16}$ has a typical metallic electrical resistivity. A superconducting transition at $T_C = 6.5$ K was observed for $\tau_2$-Ba$_3$Rh$_{15}$Ge$_{36}$ whereas $\tau_3$-Ba$_5$Rh$_{15}$Ge$_{36}$ showed metallic-like behavior down to 4 K.

1. INTRODUCTION

With the development of the phonon glass–electron crystal concept, intermetallic clathrates were considered as promising materials for thermoelectric applications. Particularly clathrate type I materials have been studied intensively, and the results have been summarized recently. Up to now, some of the most promising candidates were Ba–Ge-based solid solutions, for which it was demonstrated that transition metals such as Mn, Fe, Co, Ni, Cu, Zn, Pd, Ag, Cd, Pt, and Au can significantly stabilize a clathrate I phase deriving from the binary compound Ba$_3$Ge$_4$ which exists only in a very limited temperature range from 770 to 810 °C. Hitherto, the existence of a clathrate I Ba$_3$Rh$_4$Ge$_{16}$ was not reported. Thus, the aim of this investigation is (i) to explore the formation and homogeneity range of the corresponding clathrate I phase, (ii) to establish the phase relations in the Ge-rich part of the Ba–Rh–Ge system, (iii) to characterize the crystal structure of new ternary phases, and (iv) to provide information on the physical properties of the compounds involved. The results of density functional theory (DFT) calculations are included in order to analyze the trend of thermodynamic stability and the change of the density of states (DOS) as a function of Rh doping in the clathrate I phase Ba$_3$Rh$_{15}$Ge$_{36}$.

2. EXPERIMENTAL DETAILS

2.1. Sample Preparation and Characterization. Samples for phase analyses and crystal structures were prepared by argon arc melting from elemental ingots (Ba, 99.9 mass %; Rh, 99.99 mass %; Ge, 99.999 mass %) on a water-cooled copper hearth. To compensate for losses of Ba, ~2 wt % was added beforehand. For all samples, the weight loss was below 2 wt %. The arc-melted buttons were cut into two pieces and sealed in evacuated quartz tubes. All samples were annealed for 7 days at 750 and 700 °C and afterward characterized by powder X-ray diffraction (PXRD), differential thermal analysis (DTA), and electron probe microanalysis (EPMA). For PXRD, a Huber imaging-plate system

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Table 1. Crystallographic Data on the Solid Phases of the Binary Systems Ba–Ge (70 atom % Ge) and Rh–Ge (50 atom % Ge) and the Ternary System Ba–Rh–Ge

| phase | space group | structure type | lattice parameter [nm] | ref |
|-------|-------------|-----------------|------------------------|-----|
| Ge     | Fd3m        | Cdca            | 0.5659(7)              | 37  |
| BaGe45 | Ia3d        | BaGe13          | 2.1312(5)              | 9   |
| BaGe65 | Pmma        | BaGe3           | 1.0727(1)              | 23  |
| Rh5Ge25 <1000 | Iã2d | Rh5Ge25         | 0.5604(2)              | 38  |
| κ1-BaR8R5Ge35.75 | Pm3m | KGe23           | 1.4536(1)              |     |
| κ2-BaR8R5Ge35.75 | I4mm | BaNiSn1         | 1.4545(1)              |     |
| κ1-BaR8R5Ge35.75 | I4mm | KGe23           | 1.0693(2)              |     |
| κ2-BaR8R5Ge35.75 | I4mm | BaNiSn1         | 1.0240(3)              |     |
| κ1-BaR8R5Ge35.75 | I4mm | KGe23           | 0.458085(4)            |     |
| κ2-BaR8R5Ge35.75 | I4mm | BaNiSn1         | 0.4550(1)              |     |
| κ1-BaR8R5Ge35.75 | I4mm | KGe23           | 0.45240(3)             |     |
| κ2-BaR8R5Ge35.75 | I4mm | BaNiSn1         | 1.0274(1)              |     |
| κ1-BaR8R5Ge35.75 | I4mm | KGe23           | 0.65643(2)             |     |
| κ2-BaR8R5Ge35.75 | I4mm | BaNiSn1         | 8.04752(2)             |     |
| κ1-BaR8R5Ge35.75 | I4mm | KGe23           | 1.4725(2)              |     |
| κ2-BaR8R5Ge35.75 | I4mm | BaNiSn1         | 6.644(3)               |     |

“K-Leader”  

3. BINARY BOUNDARY SYSTEMS

For the Ge-rich part (70 atom % Ge) of the Ba–Ge system, the phase diagram reported by Okamoto17 was accepted, which was adapted from refs 18 and 19. The Rh–Ge binary system (50 atom % Ge) was taken from Massalski.20 The crystallographic data of all relevant phases are listed in Table 1. No contradictions to the accepted binary boundary systems were observed throughout all of the investigations carried out within this work.

4. RESULTS AND DISCUSSION

4.1. Clathrate I Solid Solution at 800 °C. The formation and solubility limits of the clathrate I phase BaR8R5Ge35.75₁₀, at 800 °C were studied by PXRD and EPMA on samples with nominal compositions x = 1 and y = 0. In all cases, a successful indexation of the clathrate I phase with the crystal structure of KGe23.5₈ was possible. The sample with x = 1 revealed Ge as the only secondary phase; all other samples (x ≥ 2) revealed the presence of Ge and an increasing amount of r₂ with increasing Rh content. Careful analysis of the lattice parameters and the EPMA data revealed a solubility range of Rh in BaGe₃₇₄, extending into the ternary region up to the composition BaR8R5Ge35.75₁₀ (see Figure 1). In comparison to the isovalent Co, for which a maximum solubility of 2.5 atoms/unit cell was reported,6 the solubility of the larger Rh atoms (γR₉ = 0.1345 nm and γCo = 0.1252 nm) decreases significantly but leads to a typical enlargement of the cubic lattice. The Ba content of the sample BaR8R5Ge35.85 is, according to EPMA data, slightly higher than that for the other samples, indicating a higher concentration of vacancies (□). Consistent with this observation, Rietveld refinements of the PXRD patterns—fixing the Rh content to the EPMA data—result in a composition of BaR8R5Ge35.75₁₀ for the sample with the smallest Rh content and BaR8R5Ge35.75₁₀ for all others exceeding the solubility limit. EPMA data of the as-cast alloy BaR8R5Ge35 result in a Rh content of 1.7 atom %, whereas during annealing at 800 °C, the Rh content shrinks to 1.2 atom % and superstructure reflections of BaGe₃₇₄ appear clearly observable in the powder pattern. With respect to clathrate type I (Pm₃m, α₀), BaGe₃₇₄ crystallizes in an 8 times larger unit cell (α₀ = 2α₀) with space group Ia3d because of a full order among Ge atoms and vacancies. For details, see ref 9. Rietveld refinements of the superstructure cell revealed a Rh content of 0.7 atoms/formula unit in the 24c position, which remains completely vacant.
in the fully ordered structure of binary $\text{Ba}_8\text{Ge}_{43}$. This result is in sound agreement with the 0.6 Rh atoms/formula unit found by EPMA. The as-cast sample with EPMA composition $\text{Ba}_8\text{Rh}_{0.9}\text{Ge}_{43.1}$ does not show superstructure reflections, indicating the breakdown of the vacancy ordering and a random mixture of all three species (Rh, Ge, and □) and thus a reduction of the crystal symmetry to the conventional clathrate I structure. This observation may indicate that the substitution of Ge atoms by Rh atoms, instead of exclusively filling vacant positions, starts between a Rh content of 0.6 and 0.9 atoms/formula unit (highlighted by the blue vertical line in Figure 1). The phase transition might be of second order because the symmetries of the structure and superstructure exhibit a crystallographic group–subgroup relation. Interestingly, all samples reveal a slightly higher Rh content in the clathrate phase in as-cast conditions (see Figure 1), indicating that the temperature of 800 °C is not the temperature at which the maximum solubility of Rh is reached in the clathrate I phase.

4.2. Phase Equilibria in the Ternary System Ba–Rh–Ge (>60 atom % Ge). 4.2.1. Phase Equilibria at 700 °C. The phase relations at 700 °C based on PXRD as well as EPMA data are summarized in Table S1 (Supporting Information). Corresponding micrographs representing the three-phase equilibria are shown in Figure 2. The isothermal section is drawn in Figure 3. Only one ternary phase, $\tau_1\text{BaRhGe}_3$, crystallizing in the $\text{BaNiSn}_3$ structure type, exhibits a solubility range (defined by EPMA measurements). Because the Ba content in $\tau_1\text{BaRhGe}_3$ for all measurements does not deviate significantly from 20 atom %, partial substitution of Rh by Ge in the 2a site rather than vacancy formation is suggested ($\text{Ba}_x\text{Rh}_{1-x}\text{Ge}_{3+2x}$), although in this case, the Rietveld refinement of the multiphase samples does not allow any conclusion on substitution or vacancy formation. The maximum solubility of Ge was detected in an alloy located in the three-phase region with $\tau_2$ and $\kappa_{IX}$, being $x = 0.22$. The lattice parameter $a$ is slightly increasing with increasing Ge content, whereas $c$ is slightly decreasing. Compared to the lattice parameters of the as-cast $\tau_1\text{BaRhGe}_3$ (stoichiometric composition), the unit cell volume is increased by 2%. The existence of the fully ordered structure, reported earlier, was not investigated here. For the binary phases $\text{Rh}_{1-x}\text{Ge}_2$ and $\kappa_{10}$, the solubility of the third element was below the detection limits. The three-phase equilibrium (Ge) + $\kappa_{IX}$ + $\tau_2$, as observed in sample 6 (see Figure 2), clearly documents the fact that a type I clathrate phase does not form at 700 °C. The low-temperature phase, $\text{BaGe}_2$, reported by Aydemir et al., was not observed in this investigation.

4.2.2. Phase Equilibria at 750 °C and Invariant Reactions up to 830 °C. In contrast to the isothermal section at 700 °C, the clathrate I phase $\text{Ba}_x\text{Rh}_{1-x}\text{Ge}_{46-x}$, exists at 750 °C as a truly ternary phase and extends to a maximum Rh content of $x_{\text{max}} = 1.2$ in equilibrium with $\tau_2$ and $\kappa_{IX}$ (see Figure 4). The solubility limit is practically the same as that at 800 °C. Because
the existence of binary Ba₄Ge₃X is limited to a temperature interval from 770 to 810 °C, also a lower limit of the solubility of Rh is expected and indicated in the isothermal section (Figure 4) but was not investigated. Rh stabilizes the clathrate I structure at 740 °C, where it decomposes in terms of a eutectoid reaction, κ₄⇌κ₈+τ₂, as determined by DTA measurements. Furthermore, EPMA data indicate a small solubility of Rh (0.5 atom %) in the clathrate IX phase. Similar to the results at 700 °C, a solubility range for BaRhₓGe₄₋ₓ with xₘₐₓ = 0.25 was found. The crystallographic data and compositions of the compounds for the three-phase fields are presented in Table S2 (Supporting Information), and the respective micrographs are shown in Figure 5.

Careful analyses of various samples in the as-cast state as well as after annealing at 820, 800, 775, 770, 750, and 700 °C combined with DTA measurements revealed a rather complex reaction scheme between 830 and 700 °C, yielding nine four-phase reaction isotherms (see Figure 6). The corresponding liquidus and solidus projections are illustrated in Figure 7. In Figure 8, selected micrographs of different compositions are presented. Figure 8a documents a backscatter image of sample 7 annealed at 800 °C. The DTA measurement of this alloy shows the liquidus to appear slightly above 700 °C (Figure 4), and DTA are compared, two solid-state transition-type reactions are suggested around 760 °C (U₄ and U₅ in Figure 6). Because diffusion in solid-state reactions usually is dramatically reduced compared to reactions in which a liquid phase is involved, the EPMA data as well as PXRD patterns of samples 1 and 2 at 750 °C reveal the presence of small amounts of nonequilibrium phases τ₁ and κ₄, respectively.

4.3. Crystal Structures of the Ternary Phases. 4.3.1. Crystal Structure of the Clathrate I Phase. A suitable single crystal of the clathrate I phase was selected from a sample with the maximum Rh content annealed at 800 °C. Analysis of the measured X-ray intensity data revealed isotropism with the cubic crystal structure of K₄Ge₂₃ (space group Pm̅3n). The occurrence of the necessary splitting of the 24k position (Ge₂) in Ge-based type I clathrates indicates the presence of vacancies in the neighboring 6d position, as observed also in other clathrates.⁴⁴,²⁵ As in the case of Ba₄Rh₁.₂Ge₄₂.₈, three different species (Ge, Rh, and □) are occupying the 6d site, the Rh content was fixed during the structure refinement to an EPMA value of 1.2 Rh atoms/unit cell. The atomic displacement parameters (ADPs) of the other framework positions (16i and 24k) did not infer a mixed occupancy of Rh and Ge. Thus, all Rh atoms were placed in the 6d position, and the Ge content was allowed to vary during the refinement. The results presented in Table 2 demonstrate sound correspondence of the vacancy amount in the 6d position with the occupancy of the Ge₂ atoms in the 24k position at closer distances to the vacancies. All attempts to allow anisotropic refinement of the ADPs at the 24k split position for the data set collected at 200 K led to unstable results, and therefore these positions were refined considering isotropic displacement parameters only. As summarized for several other clathrate I compounds, analysis of
temperature-dependent ADPs of guest and framework atoms allows conclusions on the lattice dynamics of the respective compound. Applying least-squares fits to the equations given by Christensen to extract Debye ($\theta_D$) and Einstein ($\theta_E$) temperatures resulted in $\theta_D = 245$ K, $\theta_{E,11} = 88$ K, and $\theta_{E,22,33} = 70$ K. These values are well within the range of the values for Ba–Ge-based clathrate I compounds reported earlier. The two Einstein temperatures originate from symmetry constraints ($U_{11}$ is different from $U_{22} = U_{33}$ for the 6c site). The Debye temperature was calculated by taking into account only ADPs of the 16i position because this crystallographic site is the only framework position unaffected by mixed occupancy or splitting. Applying the calculation method tested earlier to evaluate the thermal expansion coefficient $\alpha$ from the temperature-dependent lattice parameters $a(T)$, $\alpha_{100-300K} = 14.0 \times 10^{-6}$ K$^{-1}$ was found. The results of these analyses are displayed in Figure 9.

| Temperature | Reaction 1 | Reaction 2 |
|-------------|------------|------------|
| 815°C       | L + BaGe, ↔ k, p | 810°C L + (Ge) ↔ k, p |
| 808°C       | L ↔ k, k, k, k |  |

Figure 6. Reaction scheme (Schulz–Scheil diagram) for the Ge-rich part of the Ba–Rh–Ge system in the temperature range from 830 to 700 °C.

Figure 7. Liquidus and solidus projections of the Ge-rich part of the Ba–Rh–Ge system. The liquidus projection and primary crystallization fields of the phases are colored red, and the solidus, phases, and sample positions and numbers are colored black. The blue labels indicate the invariant reactions listed in Figure 6.

Figure 8. Selected micrographs (backscatter detector) of several samples (sample 7 was annealed at 800 °C for 1 week; all others are in the as-cast state after arc melting).
4.3.2. Crystal Structure of the Phase τ₂-Ba₃Rh₄Ge₁₆. A suitable single crystal was selected from a sample with a nominal composition of τ₂ annealed at 775 °C for 1 week. Indexation of the single-crystal X-ray diffraction data revealed a tetragonal crystal lattice with \( a = 0.65643(2) \) nm and \( c = 2.20367(8) \) nm. Analysis of the systematic extinctions prompted the extinction symbol \( I--- \) with the centrosymmetric body-centered-cubic space group \( I4/mmm \) with highest symmetry. The structure was solved by applying direct methods and refinement of seven atom sites with anisotropic ADPs converged to \( R_F = 0.0273 \) and a residual electron density of \( <2 \) e/Å³. Detailed results are listed in Table 3 and atom parameters are given in Table 4. [Interatomic distances are listed in Table S4 (Supporting Information)]. Ba atoms are located at the 2a and 4d positions.
Rh occupies the 8g site, and Ge atoms adopt the 16m, 8j, and two 4e sites. During the refinement, full ordering and full occupancy of all sites was confirmed. The composition extracted from the single-crystal analysis is in fair agreement with the EPMA results (see Table 3).

The unit cell dimensions exhibit a close relation to the BaAl4 structure type, crystallizing in the same space group symmetry: \( a = \sqrt{2} a_{\text{BaAl4}} \) and \( c = 2 c_{\text{BaAl4}} \). The 4-fold cell volume is caused by occupation of the voids and some significant shifts of the atomic sites with respect to the BaAl4 structure type. The positions of the Ba atoms are split but principally maintained; the Al1 site splits into the Ge1 and Ge2 sites. Half of the Al2 sites are occupied by the Ge3 and Ge4 atoms, while the other half is shifted along [001] and occupied by Rh atoms, which allows a new site for the Ge2 atoms and significantly different coordination figures around the two Ba sites. The coordination polyhedron of the Ba2 atoms in the 4d site with coordination number 18 is akin to the coordination polyhedron of Ba in the BaAl4 structure; only a slight distortion is observed as the Al atoms at the 4e site of BaAl4 are replaced by two 4e sites, both occupied by Ge atoms. In addition, the Rh site is located on the top and bottom of the polyhedron, forming tetragons with the Ge1 atoms (see Figure 10). Analysis of the Voronoi

### Table 3. X-ray Single-Crystal Data for Ba3Rh4Ge16 and Ba3Rh12Ge36−x (x = 0.25); (Mo Kα Radiation)

| param/compd | Ba3Rh4Ge16 | Ba3Rh12Ge36−0.75 |
|-------------|------------|-------------------|
| space group | I 4/mm (No. 139) | Fddd (No. 70) |
| structure type | Ba3Rh4Ge16 | Ba3Rh12Ge36−0.75 |
| composition from EPMA | Ba3Rh4Ge16 | Ba3Rh12Ge36−0.75 |
| composition from refinement | Ba3Rh4Ge16 | Ba3Rh12Ge36−0.75 |
| &lt;\( a \), \( b \), \( c \) [nm] | 0.66543(2), 2.20367(8), 0.84750(2), 1.4725(2), 6.644(3) |
| \( \rho_{o} \) [g/cm³] | 6.943 | 6.705 |
| max; min residual density [\( e/Å³ \)] | 1.99; –1.34 | 2.25; –2.00 |

### Table 4. Atom Parameters for Ba3Rh4Ge16 Standardized with Program Structure Tidy [Anisotropic Displacement Parameters (in \( 10^{-2} \, nm^2 \))]

| Atom Parameters | Ba in 2a (0, 0, 0) | Ge1 in 16m (x, y, z) |
|-----------------|-------------------|-------------------|
| \( U_{11} = U_{22} \), \( U_{33} \) | 0.0116(3) | 0.24358(8), 0.12878(3) |
| \( U_{12} = U_{13} \), \( U_{23} \) | 0.0082(3); 0.0083(3); 0.0116(3) | 0.24358(8), 0.12878(3) |
| \( U_{13} \) | 0.0196(8) | 0.24358(8), 0.12878(3) |
| \( U_{23} \) | 0.0171(4), 0.0155(7) | 0.24358(8), 0.12878(3) |
| \( U_{22} \) | 0.0156(4), 0.0145(7) | 0.24358(8), 0.12878(3) |
| \( U_{33} \) | 0.0118(2), 0.0113(3) | 0.24358(8), 0.12878(3) |
| \( U_{12} \) | 0.0129(3), 0.0143(5) | 0.24358(8), 0.12878(3) |

Figure 10. Crystal structure of \( \tau_2\)-Ba3Rh4Ge16. Ba atoms are colored blue, Rh green, and Ge yellow. In the projection on the (001) plane, the respective unit cell of the BaAl4 type is outlined by blue lines.
Table 5. Atom Parameters for Ba₃Rh₂₃Ge₃₆−ₓ (x = 0.25) Standardized with program Structure Tidy [39] [Anisotropic Displacement Parameters (in 10⁻² nm²)]

| Atom Parameters | Ge1a in 32h (x, y, z) | 0.0059(8); 0.0064(8); 0.20741(3) | occ, Uₚₚ | 0.55(3); 0.0154(6) |
|-----------------|----------------------|----------------------------------|----------|--------------------|
| Ge1b in 32h (x, y, z) | 0.032(1); 0.033(1); 0.20757(6) | occ, Uₚₚ | 0.15(1); 0.011(2) |
| Ge1c in 32h (x, y, z) | 0.9887(9); 0.9883(9); 0.20720(5) | occ, Uₚₚ | 0.30(1); 0.015(1) |
| Ge2 in 32h (x, y, z) | 0.0039(4); 0.01845(4); 0.006750(1) | occ | 0.933(2) |
| U₁₁ | 0.0194(4); 0.0165(3); 0.0231(4) |
| U₂₂ | 0.01080(7); 0.34855(4); 0.10461(1) |
| U₃₃ | 0.00142(2); 0.00164(3); 0.00166(3) |
| Ge3 in 32h (x, y, z) | 0.11312(7); 0.45405(4); 0.02797(1) |
| U₁₁ | 0.0173(3); 0.0150(3); 0.0219(9) |
| U₂₂ | 0.22208(7); 0.26373(4); 0.35229(1) |
| U₃₃ | 0.00173(3); 0.00151(3); 0.00177(3) |
| Ge6 in 32h (x, y, z) | 0.26417(2); 0.17143(4); 0.07278(1) |
| U₁₁ | 0.00137(3); 0.00136(3); 0.00228(3) |
| U₂₂ | 0.35578(7); 0.20218(4); 0.02998(1) |
| U₃₃ | 0.00164(3); 0.00147(3); 0.00216(3) |
| Ge8 in 32h (x, y, z) | 0.45174(7); 0.00667(4); 0.10567(1) |
| U₁₁ | 0.00148(3); 0.00153(3); 0.00170(3) |
| U₂₂ | 0.00038(1) |
| U₃₃ | 0.00129(4); 0.00163(4); 0.00180(4) |
| Ge9 in 16g (1/4; 1/4; z) | 0.00137(4); 0.00163(4); 0.00170(4) |
| U₁₁ | 0.00120(5); 0.00077(3); 0.17159(1) |
| U₂₂ | 0.00130(2); 0.00132(2); 0.00125(2) |
| U₃₃ | 0.15045(4); 0.29942(3); 0.00123(2) |
| Rh2 in 32h (x, y, z) | 0.0130(2); 0.0147(2); 0.00124(2) |
| U₁₁ | 0.00040(5); 0.00059(3); 0.001407(1) |
| U₂₂ | 0.00123(2); 0.00147(2); 0.00142(2) |
| U₃₃ | 0.36959(1) |
| Rh4 in 16g (1/2; 1/2; z) | 0.00124(3); 0.00153(3); 0.00154(3) |
| U₁₁ | 0.00037(4); 0.00122(4); 0.00020(4) |
| U₂₂ | 0.00115(4) |
| U₃₃ | 0.00177(2); 0.00143(2); 0.00197(2) |
| Ba1 in 16g (1/4; 1/4; z) | 0.56110(1) |
| U₁₁ | 0.00157(2); 0.00165(2); 0.00204(2) |
| U₂₂ | 0.00120(4); 0.00190(3); 0.00199(3) |
| Ba3 in 8a (1/4; 1/4; 1/4) | 0.00204(4); 0.00190(3); 0.00199(3) |

and sound agreement of the refined composition Ba₃Rh₂₃Ge₃₆−ₓ with the EPMA value of Ba₃Rh₂₃Ge₃₆−ₓ.

Whereas refinement of the occupancy for Ge2 resulted in a slight deficiency (occ = 0.93), the same attempt failed for Ge1 located in the 32h position with x = 0.2528, y = 0.2531, and z = 0.2929. When isotropic ADPs were applied, two rather high peaks of ~15 e Å⁻³ were detected by difference Fourier synthesis at a distance closer than 0.05 nm to the respective atom position. A detailed inspection of the electron density at this site via a difference Fourier calculation by removing the Ge1 atom revealed an elliptically shaped electron density in the two-dimensional plot parallel to the (001) plane (Figure 11). Although the three-dimensional image does not provide a clear conclusion on the splitting of this site, the improvement in the R values after splitting into two or three separate positions is significantly large (from 0.07 to 0.034 for Rₚ in both cases). The splitting into a 2-fold site with isotropic ADPs leaves a small electron density at a distance of 0.058 nm to the Ge position with higher occupancy (69%) but with no correlation to the vacancy amount of Ge2. In contrast to this observation, a 3-fold splitting results in reasonable Uₚₚ values, and even without restraining the sum of the occupancies to unity, it results in a completely filled 3-fold site, indicating that the whole electron density in this particular part of the unit cell is covered, allowing three atom positions. Moreover, the distribution of the occupancy [Table S5 and Figure S1 (Supporting Information)] over the three sites correlates with the vacancy amount at the Ge2 site. The sites Ge1a/b/c are located inside an infinite channel formed by Ge pentagons and Rh triangles [see Figure S1 (Supporting Information)]. Ge1a is located directly in the center of the triangle formed by Rh atoms, and all bonding distances are rather short compared to the other Ge–Rh distances in this structure [see Table S5 (Supporting Information)]. It seems that, whenever one of the Ge2 sites remains vacant (occ. 7%), the two Ge1 atoms close to this vacancy are shifted further away to the Ge1b site (occ. 15%), closer to the pentagonal plane formed by two Ge6, two Ge7, and one Ge9, respectively [Figure S1 (Supporting Information)]. In order to avoid the short distances to the Rh atoms, the third split site (Ge1c position) is released to the other side of the triangle closer to the pentagonal face formed by two Ge2, two Ge4, and one Ge10 [see Figure S1 (Supporting Information)].

The final refinement with anisotropic ADPs (except for Ge1a/b/c) converged to Rₚ = 0.0340 and a residual electron density of <2.3 e Å⁻³. Detailed results are listed in Table 3. There are three distinct positions for Ba atoms present in the crystal structure, and all of their coordination polyhedra are characterized by distorted faces (see Figure 12). Although the Voronoi polyhedra of Ba1 and Ba2 look similar, a detailed analysis of the Dirichlet domains using the program DIDO95 [27] revealed a slight difference in the coordination number: whereas Ba1 has 20 neighbors [neglecting two Ba2 atoms, which are contributing an area of only 1% to the domain (see the Supporting Information)], for Ba2, only 19 neighbors were identified [also neglecting two Ba1 atoms, which are contributing a small area (1.1%) to the domain; see Table S5 (Supporting Information) and Figure 12]. The entire structure is built up by blocks, which are formed by layers of polyhedra around the Ba1 and Ba2 atoms. They are alternately linked to each other by sharing pentagons. Between two of those layers the polyhedra around the Ba3 atoms are located, which are not connected via any face or atom but are linked to four neighbors via bonds to two Rh4 and two Rh5 atoms. The Ba3 polyhedra are linked to four Ba1 and four Ba2 polyhedra, two of each at the bottom and top sharing tetragons. The layers of Ba1/Ba2 polyhedra are rotated against each other by 60°. The four blocks per unit cell are shifted and rotated according to the symmetry operators of the space group Fddd. A search for the structure type (Pearson symbol: o448) in Pearson’s Crystal Data [28] prompted no results with these lattice parameters, crystal symmetry, and Wyckoff sequence, suggesting Ba₃Rh₂₃Ge₃₆−ₓ to be a unique structure type.

4.4. DFT Results. The energies of formation of Ba₃Rh₂₃Ge₃₆−ₓ for various values of x = 0–6 were derived from the DFT
calculations at zero pressure, which are shown in Figure 13. As mentioned in our previous studies, experimentally the dopants are randomly distributed over the 6d site. For the DFT calculations, the doping atoms have to be placed on specific sites within the unit cell, which, in general, causes changes of the lattice symmetry and cell shape. Therefore, to be consistent with the experiment, a cubic unit cell was enforced for all calculations. More details on the types of calculations are given in refs 29 and 30. For comparison, the enthalpies of formation for Ba8PdGe46-x and Ba8AgGe46-x,29 which were studied recently, are also shown in Figure 13. The incorporation of Ag into the Ge framework stabilizes the clathrate I compound, as evidenced by a decrease of $\Delta H$ of $-10$ kJ/mol for $x = 0-5$ (Figure 13). Further enrichment of Ag up to Ba8Ag6Ge40 does not further decrease $\Delta H$, which is in line with the solubility limits found in the experiments. In contrast to this, alloying of Rh and Pd has much more pronounced effects on the stabilization of Ba8MGe46-x. The formation energies for both compounds decrease monotonically. These unequal behaviors are attributed to the difference in pd bonding between closed and open d shell elements, which were discussed in our previous work.31

Figure 13. DFT-derived enthalpy of formation for Ba8MGe46-x (M = Rh, Pd, Ag; $x = 0-6$) and for the Ge46 framework. The information on the maximum solubility for Ba8PdGe46-x and Ba8AgGe46-x are taken from refs 40 and 29, respectively.
In order to arrive at the isovalent composition, it is assumed that each vacancy compensates four electrons, which corresponds to a valency of 1 for Rh up to about 1.2. This indicates the importance of vacancies for the solubility of Rh in the present system. The temperature dependence of the electrical resistivity of Ba₈Rh₃Ge₄₃ at about 2.0 serves as charge carriers.

4.5. Physical Properties. 4.5.1. Physical Properties of the Clathrate I Ba₈Rh₃Ge₄₂ₓₓ Ge₄₂. The temperature dependence of the electrical resistivity (ρ) as well as of the Seebeck coefficient (S) of a clathrate sample with a maximum Rh content (x = 0 to 6) is plotted in Figure 15. PXRD and EPMA analysis proved BaRhGe₃ as the main phase with traces of Ba₃Rh₄Ge₁₆ (<3%), ThCrSi₂ type (S = 33). Below 300 K, Ba₈Rh₃Ge₄₃ exhibits a temperature dependence of the electrical resistivity typically observed for metallic compounds (see Figure 16). Down to 1.8 K, no superconducting transition is observed and ρ(T) can be described up to 300 K fairly well using the Bloch–Grüneisen model (ρ_{BG} in eq 2) for metals (red solid line in Figure 16), resulting in a residual resistivity ρ₀ = 54 μΩ cm and a Debye temperature θ_D = 193 K.

4.5.2. Physical Properties of τ₁-BaRhGe₃. An as-cast sample was used for electrical resistivity measurements. EPMA analysis consistent with the Rietveld refinement proved BaRhGe₃ as the main phase with traces of Ba₃Rh₄Ge₁₆ (<3%), ThCrSi₂ type (S = 33). Below 300 K, Ba₈Rh₃Ge₄₃ exhibits a temperature dependence of the electrical resistivity typically observed for metallic compounds (see Figure 16). Down to 1.8 K, no superconducting transition is observed and ρ(T) can be described up to 300 K fairly well using the Bloch–Grüneisen model (ρ_{BG} in eq 2) for metals (red solid line in Figure 16), resulting in a residual resistivity ρ₀ = 54 μΩ cm and a Debye temperature θ_D = 193 K.

4.5.3. Physical Properties of τ₁-Ba₈Rh₃Ge₄₃. The electrical resistivity of Ba₈Rh₃Ge₄₃ was measured in the temperature range from 300 mK to 300 K. The resistivity vanishes at T_C = 6.5 K, indicating a transition into a superconducting state. Above T_C, the resistivity data exhibit a simple metallic temperature dependence. The residual resistivity ratio from room temperature to 2.0 serves as charge carriers.

In order to get a rough estimation of the charge carrier density, Mott’s formula 1 was employed, giving the diffusion thermopower in terms of a free electron model:

$$S_D(T > \theta_D) = \frac{\pi^2 k_B^2 m_e}{3 e^2} T$$

where $m_e$ is the electron mass and $e$ is the carrier charge. A linear fit to $S(T)$ resulted in a charge carrier density $n$ of $\sim 10^{21}$ cm⁻³. This value is in rather sound agreement with $1.6 \times 10^{21}$ cm⁻³, resulting from a simple calculation assuming that the two uncompensated electrons/unit cell [a = 10.6932(2) nm] for Ba₈Rh₃Ge₄₂ₓₓ serve as charge carriers.

Figure 14. DFT-derived DOSs for Ba₈Rh₆₋ₓ Geₓ (x = 0 to 6). Energy scale with respect to the Fermi energy.

Figure 15. Electrical resistivity $\rho$ and Seebeck coefficient $S$ of Ba₈Rh₃Ge₄₂ₓₓ as a function of the temperature. The solid black line represents a linear fit to the $S$ data.

Figure 16. Electrical resistivity $\rho$ as a function of the temperature for τ₁-Ba₈Rh₃Ge₄₃. The solid line displays the results of a least-squares fit to the Bloch–Grüneisen model.
scattering on Rh atoms in the sense of Mott and Jones has been taken into account but does not seem to possess any significant contribution. However, the results can be accounted for in terms of the parallel resistor model:\textsuperscript{34}

\[
\frac{1}{\rho(T)} = \frac{1}{\rho_{BG}(T)} + \frac{1}{\rho_{\text{max}}}
\]

with \(\rho_{BG}(T) = \rho_0 + R \left( \frac{T}{\theta_D} \right)^5 \)

\[
\int_0^{\theta_D/T} \frac{z^5}{(e^z - 1)(1 - e^{-z})} \, dz
\]

(2)

In this model, \(\rho_{BG}\) is the Bloch–Grüneisen term and \(\rho_{\text{max}}\) the saturation resistivity. A least-squares fit reveals a residual resistivity of \(\sim 23 \, \mu\Omega \, \text{cm}\) and a saturation resistivity of \(\sim 321 \, \mu\Omega \, \text{cm}\) (shown as a solid line in Figure 17). As a result, a Debye temperature of \(\sim 145 \, \text{K}\) was determined. Employing the empirical model of McMillan leads to an electron–phonon coupling constant \(\lambda_{\text{ep}} \approx 0.9\), indicating a value beyond the BCS weak-coupling limit. Resistivity measurements were carried out in various external fields also. With increasing magnetic field, the transition temperature shifts to lower values until the superconducting state is completely suppressed at 1.5 T in the temperature range available (inset Figure 17). A commonly used 90/10 technique, i.e., the midpoint between 90\% of \(\rho_0\) and 10\% of \(\rho_0\) determines the superconducting transition temperature. Results are collected in Figure 18. The initial slope of the upper critical field is derived as

\[
- \frac{\partial H_{c2}}{\partial T} \bigg|_{T=T_c} = 0.253
\]

(3)

The model by Werthamer et al.\textsuperscript{35} (WHH) is used to describe the temperature dependence of the upper critical field (red solid line in Figure 18). This model takes into account the spin–orbit scattering (\(\lambda_{\text{so}}\)), causing the electron spin to no longer be a good quantum number, and the depairing mechanism due to Zeeman splitting, called the Pauli limiting (PL). Quantitatively, two parameters guide this model, i.e., the Maki parameter\textsuperscript{36} and the spin–orbit interaction constant. The Maki parameter can be estimated from

\[
\alpha = 5.35 \times 10^{-5} H_{c2}^4 \cdot 10000 = 0.135
\]

(4)

This small value hints to a rather limited influence of the PL and, therefore, the establishment of orbital depairing to play the essential role in this material. The WHH model predicts an upper critical field of 1.14 T. An alternative route to derive \(\alpha\) follows from\textsuperscript{35}

\[
\alpha = \frac{e^2 h}{2 m_e \gamma^2 k_B} = 0.139
\]

(5)

where \(e\) is the electron charge, \(m_e\) the electron mass, \(\gamma\) the Sommerfeld value, and \(\rho_0\) the residual resistivity. The Maki parameter obtained from eq 5 coincides very well with that derived from eq 4. Details on the superconducting state of \(\tau_2\)-Ba\(_3\)Rh\(_4\)Ge\(_{16}\) will be presented in a future publication.

**Heat Capacity of \(\tau_2\)-Ba\(_3\)Rh\(_4\)Ge\(_{16}\).** Specific heat measurements were performed from 2 to 80 K in magnetic fields from 0 to 2 T, and the results are displayed as \(C_p/T\) versus \(T\) in Figure 19. In zero fields, a sharp second-order transition occurs...
at around 6.7 K, confirming the superconducting transition. In conjunction with the heat capacity anomaly at $T = T_C$, bulk superconductivity can be concluded. The electronic Sommerfeld coefficient ($\gamma$) is about 80 mJ/molK². The $H_C$ behavior extracted from the field dependence of the superconducting specific heat anomaly fits well to the results obtained from electrical resistivity measurements. The ratio of the superconducting specific heat jump to the normal state heat capacity $\gamma T_C$ yields

$$\frac{\Delta C_p(T_C)}{\gamma T_C} \approx 1.38$$

which is close to the BCS value of 1.43. The inset of Figure 19 shows the field dependence of the jump at $T_C$.

4.5.4. Physical Properties of $\tau_3$-Ba$_3$Rh$_4$Ge$_{35.75}$

The electrical resistivity from 4 to 300 K is plotted in Figure 20.

![Figure 20. Electrical resistivity $\rho$ as a function of the temperature for $\tau_3$-Ba$_3$Rh$_4$Ge$_{35.75}$. The solid line represents a least-squares fit to the model described in the text.](image)

The temperature dependence is metallic-like, and in contrast to Ba$_3$Rh$_4$Ge$_{60}$, no superconductor transition was observed to 4.1 K. At elevated temperatures, the slope of the electrical resistivity significantly deviates from the simple linear temperature dependence and can be well described by applying the parallel resistor model (eq 2). Using this model to fit the data, residual resistivity $\rho_0 = 320 \mu\Omega$ cm, saturation resistivity $\rho_{sat} = 784 \mu\Omega$ cm, and Debye temperature $\Theta_D = 150$ K were extracted. Measuring the Seebeck coefficient at room temperature revealed electrons to be the main charge carriers and the value of $-6 \mu$V/K is relatively small, as expected for metals and intermetallic compounds.

5. CONCLUSIONS

Although the solubility of Rh is rather limited, Rh was found to stabilize a clathrate phase of type I, Ba$_3$Rh$_4$Ge$_{60-\gamma}$. The homogeneity range at 800 °C extends to a Rh content of 1.2 atoms/unit cell at a remaining vacancy content of $\gamma = 2$, accompanied by an increase of the lattice parameter to $a = 1.06932(2)$ nm. Investigating the lattice dynamics of this compound using single-crystal X-ray data revealed features similar to that already reported for other Ge-based clathrates. Phase relations in the Ge-rich part of the Ba–Rh–Ge system are characterized by the existence of two novel compounds, Ba$_3$Rh$_4$Ge$_{60}$ and Ba$_3$Rh$_4$Ge$_{35.75}$ for both of which a new, unique crystal structure was established by single-crystal X-ray measurements.

The DFT-derived enthalpies of formation for Ba$_3$Rh$_4$Ge$_{60-\gamma}$ support the experimental results, namely, that the incorporation of Rh atoms into the clathrate I framework significantly stabilizes the compound. The DOSs reveal gaps or deep minima, which are linked to the large gap of Ba$_3$Ge$_{66}$ about 1 eV below $E_F$. The Fermi energy gets closest to a deep minimum for $x = 3$, in line with the valence electron-counting rule, which yields $x_{e_{\text{sp}}}=16/5$ for the critical concentration.

The limited homogeneity range of Ba$_3$Rh$_4$Ge$_{60-\gamma}$ prevents this compound from exhibiting interesting thermoelectric properties because the sample with the maximum Rh content, Ba$_3$Rh$_{1.2}$Ge$_{42.8}$, still has metallic properties and thus the Seebeck coefficient of $-20 \mu$V/K at room temperature remains below thermoelectrically interesting values. The electrical resistivities of BaRhGe$_3$ and Ba$_3$Rh$_{13}$Ge$_{35.75}$ increase with increasing temperature, exhibiting metallic behavior, and for Ba$_3$Rh$_{13}$Ge$_{35.75}$, revealing a 6 times higher residual resistivity $\rho_0$ (320 $\mu$Ω cm), a tendency for saturation above 300 K is observed. Ba$_3$Rh$_{13}$Ge$_{46}$ shows a superconducting transition at a critical temperature of $T_C = 6.5$ K and the upper critical field is completely suppressed at 1.5 T, close to the predicted value of 1.14 T from the WHH model. The heat capacity data confirmed bulk superconductivity and BCS-like behavior.

### ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format and additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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