The Intermetallic Type-I Clathrate $Na_8Zn_4Ge_{42}$

Saskia Stegmaier,[a] Viktor Hlukhyy,[a] and Thomas F. Fässler*[a]

Dedicated to Professor Juri Grin on the Occasion of His 65th Birthday

Abstract. The new intermetallic type-I clathrate $Na_8Zn_4Ge_{42}$ was obtained by direct reaction of the elements, and its crystal structure was determined by means of single-crystal X-ray diffraction methods. The structure is described in space group $Pm\bar{3}n$ (no. 223) with $a =$ 10.6982(1) Å. A mixed Zn/Ge occupancy is found for one of the network sites ($6c$). $Na_8Zn_4Ge_{42}$ represents an air-stable electron-precise Zintl phase with exclusively Na cations located in the cavities of a polyanionic host network of four-connected Zn and Ge atoms.

Introduction

Clathrates owe their name to host frameworks featuring cavities in which guests can be accommodated. Among the representatives of host-guest systems with clathrate-type structures there are as different materials as gas hydrates, clathrasils/zeolites or semiconducting/intermetallic clathrates. The chemistry and properties of the latter have been highlighted recently.[1–4] The most common clathrate host structures, namely those of type-I ($cP46$) and type-II ($cF136$), are built of four-connected networks. Generally, networks with covalent bonds between tetrahedrally connected atoms are native to the structural chemistry of the group 14 elements C, Si, Ge, and Sn.

The suitability of empty clathrate networks as structures of (metastable) allotropes of group 14 elements is substantiated by the (almost) guest-free type-II clathrates Na_xSi_{136} ($x < 1$)[5,6] and $\square_{24}Ge_{136}$[7,8] ($\square$: vacant position). In case of the so-called "intermetallic" or "semiconducting" clathrates of Si, Ge and Sn, the cavities are occupied by electropositive alkali metal (A), alkaline earth metal (Ae), or rare earth metal atoms. The phases are described as polar intermetallics or electron-precise Zintl compounds with cations in the cages of a polyanionic framework structure. A formally charge-balanced situation with a framework structure in accord with the 8-N rule can be achieved either via vacancies or via the partial substitution of group 14 (Tt: tetrel element) atoms by electron-poorer group 13 (Tr: triel element) or late d-block metal (T) atoms on network sites. Note that one vacancy is

* Prof. Dr. T. F. Fässler
  E-Mail: Thomas.Faessler@lrz.tum.de
[a] Department of Chemistry
  Technische Universität München
  Lichtenbergstraße 4
  85747 Garching, Germany

associated with four (3b-Tt^-) atoms on the neighboring positions (3b: three-bonded).

Among the type-I clathrates, for example, binary $A_8Tt_{44}\square_2$ and $Ae_8Tt_{42}\square_4$ as well as ternary $A_8Tr_8Tt_{38}$ and $Ae_8Tr_{16}Tt_{30}$ are thus electron-precise Zintl phases. The current interest in such intermetallic clathrates is mainly due to the promising thermoelectric properties of some representatives; e.g. for $Ba_8Ga_{16}Ge_{30}$ considerably high ZT (Figure of merit) values have been reported.[9–11] A conceptual approach to an understanding of the potential of the intermetallic clathrates as thermoelectric materials is provided by the PGEC (phonon-glass and electron-crystal) concept.[12] In addition some type-I clathrates such as $K_8Al_8Si_{38}$ with a quasi-direct bandgap of ca. 1 eV are promising materials for solar energy conversion.[13]

In this context, and in view of other four-connected network structures found within the Sn-rich ternary Na-Zn-Sn phases,[14,15] we investigated the Ge-rich side of the Na-Zn-Ge system. Already known type-I clathrates of Ge or Sn with alkali metal atoms as guests and group 12 element atoms ($T =$ Zn, Cd, or Hg) on framework sites include $K_8Zn_xGe_{46-x}$,[16] $A_8Zn_xSn_{46-x}$ with $A =$ K,[17–19] Rb,[19,20] and Cs,[19–21] $Cs_8Cd_xSn_{46-x}$,[22] $A_8Hg_xGe_{46-x}$ with $A =$ K and Rb,[23] as well as $A_8Hg_xSn_{46-x}$ with $A =$ K, Rb and Cs.[24] Generally, these phases are described as electron-precise Zintl compounds with the ideal composition $A_8T_4Tt_{42}$, except for the Hg-substituted Ge clathrates, which are reported to have an (approximate) composition of $A_8Hg_3Ge_{43}$. In most type-I clathrates with Si and Zn as the framework atoms, a mixed occupation of the framework sites is observed at the crystallographic Wyckoff site $6c$, whereas in $K_8Zn_{3.5}Si_{42.5}$ and $Rb_{7.9}Zn_{3.6}Si_{42.4}$[25] an Si vs. Zn substitution occurs also at the $24k$ site.

Another type-I clathrate with $Tt =$ Ge and $T =$ Zn (besides $K_8Zn_xGe_{46-x}$[16] mentioned above) is $Ba_8Zn_8Ge_{38}$.[26] Na atoms in guest positions are less frequent but are found in $Rb_6Na_2Ge_{44.89}$, $Cs_6Na_2Zn_4Ge_{42}$ and $Cs_{6.40}Na_{1.60}Ga_8Ge_{38}$,[27] as well as in $Na_8Tr_xGe_{46-x}$ with $Tr =$ Al and Ga.[28] Notably, a binary $A_8Ge_{46-y}\square_y$ phase with $A =$ Na has not been reported, and Na is generally considered not to fit well in the larger cages of a Ge type-I clathrate host framework.[1] The existence of clathrates $K_8Li_xGe_{44-x/4}\square_{2-3x/4}$ with the lower

homologue Li has been reported; however, Li does not occupy positions within the polyhedral cages but substitutes Ge in the host framework.[29–31] Recently various polycrystalline $K_xBa_{8-x}Zn_yGe_{46-y}$ clathrates were investigated in which Zn was observed to mix with Ge only at one specific Ge atom site. In this context the band structure of hypothetical electron-precise $Na_8Zn_4Ge_{42}$ was calculated and found to be a semiconductor with a bandgap of ca. 0.5 eV.[32] Herein we present now the type-I clathrate $Na_8Zn_4Ge_{42}$, which exclusively contains the alkali metal Na as guest atoms.

Experimental Section

Synthesis: For the synthesis of the title compound, all materials were handled in argon atmosphere using an argon-filled glove box and other standard inert gas techniques. Ge pieces (99.999%, ChemPur) and Zn granules (Merck) were used as received, Na was purified by liquating. The samples were sealed in niobium or tantalum ampoules, these ampoules were placed in silica tubes which were then evacuated, sealed, and inserted in a vertical resistance tube furnace.

$Na_8Zn_4Ge_{42}$ was first obtained by direct reaction of the elements in a Na:Zn:Ge ratio of 2:1:5. 0.078 g of Na, 0.110 g of Zn and 0.612 g of Ge were sealed in a tantalum ampoule, heated to 650 °C and kept at this temperature for two days. Then the furnace was turned off, and the sample was removed from the furnace after it had cooled to room temperature. Powder XRD analysis of the product showed the presence of the type-I clathrate $Na_8Zn_4Ge_{42}$ and of α-Ge, accompanied by some unindexed reflections. The latter were not observed in the powder XRD pattern of a sample that was exposed to air and are thus attributed to at least one unidentified air-sensitive phase. $Na_8Zn_4Ge_{42}$ is air-stable. After the characterization of $Na_8Zn_4Ge_{42}$ by means of single crystal XRD structure analysis, the title phase was also synthesized using stoichiometric amounts of the elements. However, in this case no phase-pure samples were obtained. For example, the reaction of 0.053 g of Na, 0.075 g of Zn and 0.873 g of Ge using a temperature program analogous to that described above but with isothermal dwelling for six days, led to $Na_8Zn_4Ge_{42}$ as the main phase, beside small amount of elemental germanium (Supporting Information). The air-sensitive impurity mentioned above may also occur.

Powder X-ray Diffraction: For powder XRD analysis the samples were finely ground, optionally diluted with diamond powder, and sealed in glass capillaries in an argon-filled glove box. To test their air stability the samples were exposed to air and measured in transmission mode. Powder XRD data were collected with a STOE STADI P powder diffractometer equipped with an imaging plate and a linear position sensitive detector (IP-PSD, and L-PSD) using Cu-$K_{\alpha1}$ radiation [λ = 1.54060 Å, curved Ge (111) monochromator]. The STOE WINXPOW program package[33] was used for phase analysis.

Single Crystal X-ray Diffraction and Crystal Structure Determination: Block-shaped, dark-silver, lustrous crystals of $Na_8Zn_4Ge_{42}$ were selected under a microscope and in ambient atmosphere. A suitable single crystal was fixed on a glass fiber and mounted on the goniometer head of a BRUKER APEX II diffractometer system (KAPPA goniometer, APEX II CCD detector). Single crystal XRD data were collected at 293 K using Mo-K_{α} radiation (λ = 0.71073 Å, graphite monochromator, rotating anode source). The BRUKER SAINT software was used for data processing, including an absorption correction with SADABS. XPREP[34] was used for space group determination, SHELXS[35,36] for structure solution (Direct Methods) and SHELXL[37,38] for structure refinement (full-matrix least-squares on F_o^2). The structure was solved in space group $Pm\bar{3}n$ (no. 223). Selected crystallographic data and refinement details are given in Table 1, Table 2, and Table 3. Refinement cycles with a free variable for the occupancy parameter of the Na1 (2a) and Na2 (6d) sites, showed that both positions are fully occupied. A mixed Zn/Ge occupancy was tested in separate refinement cycles for all three network sites (6c, 16i and 24k), showing that Zn only occupies the 6c site. A free refinement of the occupancy parameters for Zn and Ge on this site (with the sum fixed to 1) led to an occupancy parameter of 0.31(5) for Ge, which is close to the ideal Zn:Ge ratio of 2/3:1/3 for the 6c site and corresponds to the Zintl phase composition $Na_8Zn_4Ge_{42}$. In the final refinement

Table 1. Selected crystallographic, data collection, and refinement data for $Na_8Zn_4Ge_{42}$.

	$Na_8Zn_4Ge_{42}$
Formula weight, M /g·mol^{-1}	3494.18
Space group	$Pm\bar{3}n$ (no. 223)
Z	1
Unit cell parameter, a /Å	10.6982(1)
Unit cell volume, V /Å^3	1224.4(1)
Calculated density, ρ_{calc} /g·cm^{-3}	4.739
Absorption coefficient (Mo-K_{α}), μ /mm^{-1}	27.30
$F(000)$	1552
Crystal color, shape	Dark-silver lustrous, block
Temperature, T /K	293
Wavelength (Mo-K_{α}), λ /Å	0.71073
Θ range /°	2.69 to 31.40
Limiting indices	$-15 \le h \le 15$
	$-15 \le k \le 15$
	$-15 \le l \le 14$
Reflections / unique	12469 / 395
Completeness /%	100
R_σ, R_{int}	0.009, 0.030
Data / restraints / parameters	395 / 1 / 17
Extinction coefficient	0.0020(1)
Residual map / e Å^{-3}	+0.691 and –0.621
Goodness-of-fit on F^2	1.29
R_1, wR_2 [$I > 2\,\sigma(I)$]	0.011 / 0.025
R_1, wR_2 (all data)	0.011 / 0.025

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for $Na_8Zn_4Ge_{42}$.

Atom	Wyck.	Occ.	x	y	z	U_{eq} /Å$^{2\ a)}$
			$Na_8Zn_4Ge_{42}$			
Zn/Ge1	6c	2/3:1/3 $^{b)}$	1/4	0	1/2	0.0114(1)
Ge2	16i		0.18299(1)	x	x	0.01002(8)
Ge3	24k		0	0.30920(2)	0.11683(2)	0.01049(8)
Na1	2a		0	0	0	0.0348(9)
Na2	6d		1/4	1/2	0	0.142(3)

a) U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. b) Occupancy factors fixed in final refinement steps, see Experimental Section.

Table 3. Anisotropic displacement parameters (U_{ij} /Å^2) for $Na_8Zn_4Ge_{42}$.

Atom	U_{11}	U_{22}	$Na_8Zn_4Ge_{42}$ U_{33}	U_{23}	U_{13}	U_{12}
Zn/Ge1	0.0129(2)	0.0106(1)	U_{22}	0	0	0
Ge2	0.01002(8)	U_{11}	U_{11}	−0.00049(5)	U_{23}	U_{23}
Ge3	0.0108(1)	0.0111(1)	0.0096(1)	−0.00057(7)	0	0
Na1	0.0348(9)	U_{11}	U_{11}	0	0	0
Na2	0.098(5)	0.163(4)	U_{22}	0	0	0

steps the ratio was thus fixed to this ideal value. The same Zn:Ge ratio was determined from the single crystal XRD structure analysis using crystals of $Na_8Zn_4Ge_{42}$ obtained from reactions of the elements in different ratios.

Further details of the crystal structure investigations may be obtained from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk) on quoting the depository number CSD-1953129 for $Na_8Zn_4Ge_{42}$.

EDX Measurements: EDX analyses of single crystals of $Na_8Zn_4Ge_{42}$ (unit cell determined by single crystal XRD previous to EDX analysis) were carried out using a JEOL 5900LV scanning electron microscope equipped with an OXFORD INSTRUMENTS INCA energy dispersive X-ray microanalysis system. The qualitative analysis showed the presence of Na, Zn and Ge, and the absence of other elements heavier than Na (Supporting Information).

Supporting Information (see footnote on the first page of this article): Figure of powder X-ray diffractogram of "$Na_8Zn_4Ge_{42}$" sample; Table with result of the EDX analysis of $Na_8Zn_4Ge_{42}$ single crystal.

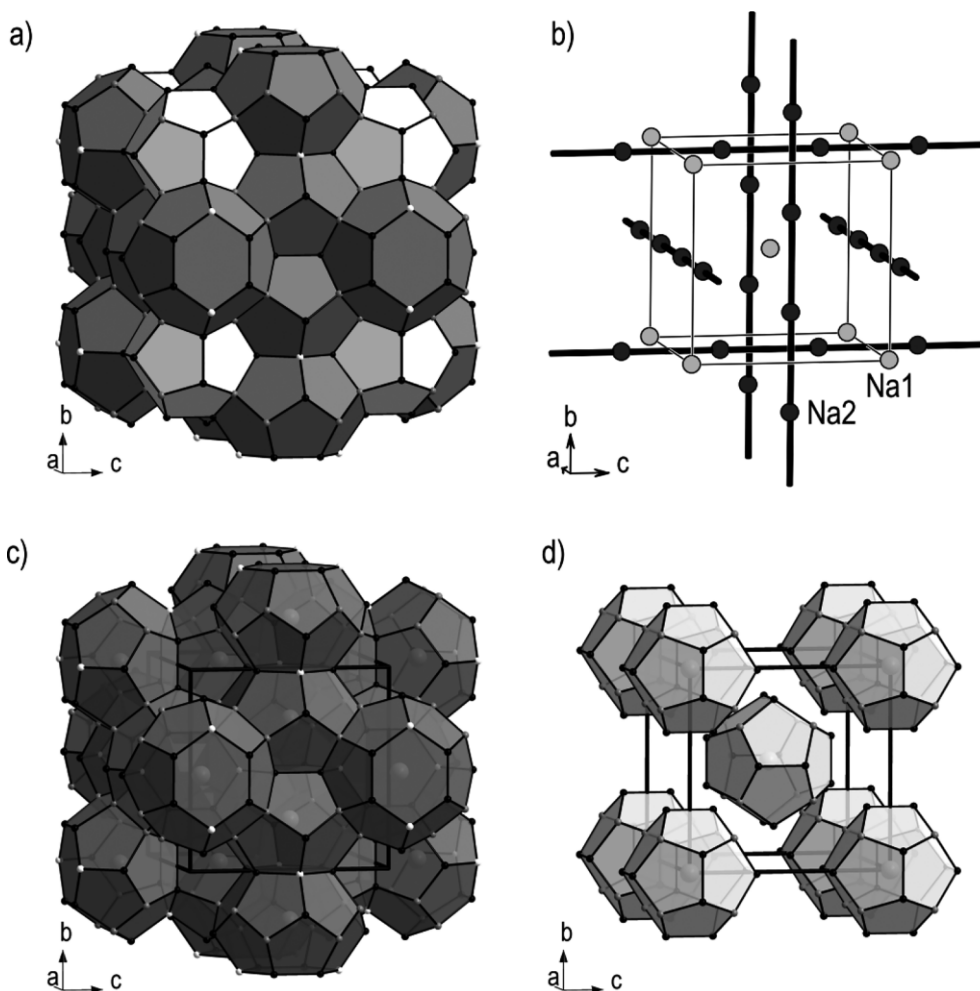**Figure 1.** Crystal structure of the intermetallic type-I clathrate $Na_8Zn_4Ge_{42}$. (a) Space-filling arrangement of tetrakaidecahedra (dark gray) and pentagonal dodecahedra (light gray). (b) A15-style arrangement of the guest sites. The connecting lines between the positions Na2 indicate the rod packing that describes the alignment of the columns of the tetrakaidecahedra which share hexagonal faces. (c) Separate drawing of the arrangement of tetrakaidecahedra. (d) Separate drawing of the bcc-like array of pentagonal dodecahedra.

Results and Discussion

$Na_8Zn_4Ge_{42}$ adds to the group of intermetallic ternary $A_8T_xTt_{46-x}$ type-I clathrates (space group $Pm\bar{3}n$, no. 223) of the tetrel elements (Tt) Ge and Sn with group 12 element atoms (T) in the framework and alkali metal atoms (A) as guests (Figure 1a). As such, the title phase shows a host framework structure of tetrahedrally four-bonded atoms on 6c (Zn/Ge1), 16i (Ge2) and 24k (Ge3) sites, which contains two types of cavities. The corresponding two guest sites (2a and 6d) in the center of the cages are arranged in an A15 (Cr_3Si) type structure (cf. Figure 1b). The coordination polyhedra of the Na cages are pentagonal dodecahedra and tetrakaidecahedra for Na1 (on 2a) and Na2 (on 6d), respectively. The 20 vertices of a pentagonal dodecahedron (with twelve pentagonal faces) comprise eight Ge2 (16i) and twelve Ge3 (24k) positions, and a 24-vertex tetrakaidecahedron with twelve pentagonal and two hexagonal faces is built of four Zn/Ge1 (6c), eight Ge2 (16i) and twelve Ge3 (24k) positions (see Figure 2).
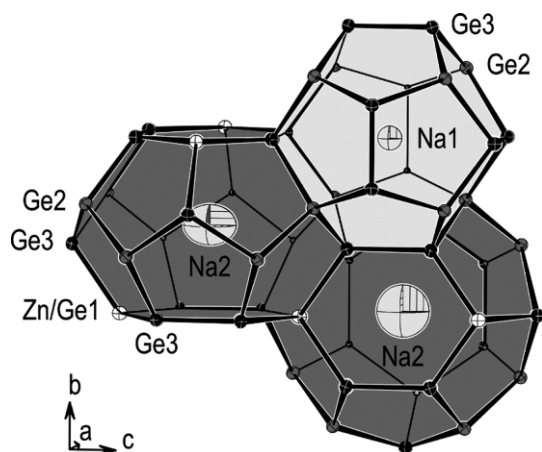

Figure 2. Representation of a section of the crystal structure of $Na_8Zn_4Ge_{42}$. Displacement ellipsoids are drawn at a 70 % probability level.

The type-I clathrate structure can be described as a space-filling arrangement of these polyhedra as shown in Figure 1a. Separate drawings of the arrangement of the tetrakaidecahedra and pentagonal dodecahedra are depicted in Figure 1c and d, respectively. Columns of tetrakaidecahedra are aligned in a rod packing manner as schematically shown in Figure 1b (connecting lines between Na2 positions), and the pentagonal dodecahedra take the remaining space, thereby forming a *bcc* (body

centered cubic) like array, see Figure 1d and b (Na1 positions). A tetrakaidecahedron shares its two hexagonal faces with adjacent tetrakaidecahedra of the same column, eight pentagonal faces with other tetrakaidecahedra of columns that run perpendicularly, and four pentagonal faces with pentagonal dodecahedra.

The displacement parameters for the network atoms of $Na_8Zn_4Ge_{42}$ are small (see Table 3 and Figure 2), as it is generally observed for intermetallic clathrates and typical for rigid frameworks of covalently bonded atoms. By contrast, large displacement parameters for the Na atoms are found, especially for Na2 (on 6d) in the larger cages (see also Table 3 and Figure 2). The displacement parameters of the guest atoms in intermetallic clathrates are associated with their "rattling" in the cages, and the differences between the parameters for the atoms in the 20- and 24-vertex cages is also a common feature of the type-I clathrates. For $Na_8Zn_4Ge_{42}$ the ratio of $U_{eq}(Na2):U_{eq}(Na1)$ is approx. 4.1, comparable, for example, to the situation of the K atoms in $K_8Hg_4Sn_{42}$.[24] In the clathrate Na_8Si_{46} with its smaller Si-cages the displacement parameters of the guest Na atoms are already significantly larger than those of the Si atoms of the host framework.[39]

Therefore it is not surprising that for the title compound $Na_8Zn_4Ge_{42}$ with its larger cages the ADP values of the Na guest atoms are so large. In the series of $A_8T_xTt_{46-x}$ phases with the same T and Tt but different A atoms, the structures with the larger alkali metals generally show smaller displacement parameters of the A atoms and also smaller differences between the parameters for $A1$ and $A2$.[23,24] Another characteristic feature concerning the displacement parameters is the symmetry-constrained isotropic behavior of Na1 (2a) in the pentagonal dodecahedra, which is in contrast to the pronounced anisotropy found for Na2 (6d) in the tetrakaidecahedra, and relates to the different shapes of the polyhedra (cf. Figure 2 and Na–Ge and Na–Zn/Ge interatomic distances given in Table 4). For $Na_8Zn_4Ge_{42}$ the ratio $U_{22}(Na2):U_{11}(Na2)$ is approx. 1.7 and thus again similar to the corresponding ratio for related phases.[23,24]

The interatomic distances in the Zn–Ge network are in the narrow range from 2.481(1) to 2.500(1) Å, that is only slightly longer than the interatomic distance in α-Ge (2.445 Å) or the sum of covalent radii for Zn and Ge (2.42 Å; according to reference[40]). With the exception of the bond angle Zn/Ge1–Ge3–Ge3 of 124.9° in the six-membered rings (hexagonal faces of the tetrakaidecahedra), all other bond angles in the

Table 4. Interatomic distances for $Na_8Zn_4Ge_{42}$.

Atoms		Mult.	Distance /Å	Atoms		Mult.	Distance /Å
Zn/Ge1	–Ge3	4×	2.4893(2)	Na1	–Ge2	8×	3.3908(3)
	–Na2	4×	3.7824(1)		–Ge3	12×	3.5361(2)
Ge2	–Ge2	1×	2.4833(5)	Na2	–Zn/Ge1	4×	3.7824(1)
	–Ge3	3×	2.4812(1)		–Ge2	8×	3.9810(1)
	–Na1	1×	3.3909(3)		–Ge3	8×	3.5891(1)
	–Na2	3×	3.9810(1)		–Ge3	4×	4.1479(2)
Ge3	–Ge3	1×	2.4996(4)				
	–Na1	1×	3.5361(2)				
	–Na2	2×	3.5892(1)				

ZAAC
Journal of Inorganic and General Chemistry
Zeitschrift für anorganische und allgemeine Chemie

ARTICLE

framework are between 104.2° and 111.1° and thus close to the ideal tetrahedral angle of 109.5°.

As for related intermetallic clathrates, the exact composition of the title phase is also an issue to be discussed. In the structure refinement on the basis of single crystal XRD data, a mixed Zn/Ge occupancy was found only for the $6c$ network site. The free refinement of the occupancy parameters for Zn and Ge on this site (with the sum fixed to 1) led to a Zn:Ge ratio close to 2/3:1/3 resulting in the Zintl phase composition $Na_8Zn_4Ge_{42}$. Despite the similar number of electrons of Ge and Zn the refinements show significant differences, but as a matter of fact, the discussion of mixed site occupancy is disputable in structures with atoms that have almost the same atomic number like Zn and Ge. The description of the title phase as $Na_8Zn_4Ge_{42}$ with Na cations and a polyanionic network of formally isoelectronic (4b-Zn^{2-}) and (4b-Ge^0) atoms (4b: four-bonded) is in accord with previous findings for related phases (cf. Introduction). The $A_8T_xTt_{46-x}$ type-I clathrates (space group $Pm\bar{3}n$, no. 223) with group 12 element atoms show a mixed T/Tt occupancy exclusively on the $6c$ site, and with the exception of the A–Hg–Ge clathrates they are all described as electron-precise Zintl compounds with formula $A_8T_4Tt_{42}$.

In this context, one may discuss different ways to reach electron-precise compositions for these ternary phases. Provided that the two guest sites are fully occupied by alkali metal atoms (which is generally found to be the case and can be determined reliably on the basis of XRD data), there is exactly one value for x that corresponds to an electron-precise Zintl phase $A_8T_xTt_{46-x}$ with full occupancy of all framework sites ($x = 4$ for group 12 elements T = Zn, Cd, Hg). However, there is also the possibility that there are both T atoms and vacancies besides the Tt atoms in the framework giving the formula $A_8T_xTt_{46-x-y}\square_y$, which opens another way to reach a charge-balanced situation which even includes the possibility of a homogeneity range. (Note that in case of the binary A_8Tt_{46-x} phases the vacancies also occur at the site $6c$.) With group 12 element atoms all compositions $A_8T_xTt_{46-x-y}\square_y$ that meet the condition $2x+4y = 8$ (or $x = 4-2y$) qualify as Zintl phases with formally eight A^+ cations, x (4b-T^{2-}) and $y \times 4$ (3b-Tt^-) [since there are four (3b-Tt^-) per vacancy]. The occurrence of a phase width has been studied, for example for $Ba_8Zn_xGe_{46-x-y}\square_y$ and related phases.[26,41]

Conclusions

$Na_8Zn_4Ge_{42}$ is another example of an intermetallic ternary $A_8T_xTt_{46-x}$ type-I clathrate and can be described as an electron-precise Zintl phase with Na cations in the voids of a polyanionic host framework of four-bonded Zn and Ge atoms. This phase thus shows that a Ge-based type-I clathrate framework with encaged A atoms can also be realized with the light alkali metal Na. The only other known Ge-based type-I clathrates with Na atoms as guests are the $Na_8Tr_xGe_{46-x}$ phases with Tr = Al and Ga,[28] and thus, $Na_8Zn_4Ge_{42}$ also evidences the close relation between the structural chemistry of alkali metal-

zinc-tetrelides and that of related alkali metal-trielide-tetrelides.

References

[1] a) A. J. Karttunen, T. F. Fässler, M. Linnolahti, T. A. Pakkanen, *Inorg. Chem.* **2011**, *50*, 1733–1742; b) A. J. Karttunen, T. F. Fässler, *ChemPhysChem.* **2013**, *14*, 1807–1817.
[2] A. V. Shevelkov, K. Kovnir, in: *Zintl Phases: Principles and Recent Developments* (Ed.: T. F. Fässler), Springer-Verlag, Berlin, **2011**, pp. 97–142.
[3] M. Ångqvist, P. Erhart, *Chem. Mater.* **2017**, *29*, 7554–7562.
[4] M. Baitinger, B. Bohme, A. Ormeci, Y. Grin, in *Physics and Chemistry of Inorganic Clathrates*, vol. 199 (Ed.: G. S. Nolas), **2014**, pp. 35–64.
[5] J. Gryko, P. F. McMillan, R. F. Marzke, G. K. Ramachandran, D. Patton, S. K. Deb, O. F. Sankey, *Phys. Rev. B* **2000**, *62*, R7707.
[6] A. Ammar, C. Cros, M. Pouchard, N. Jaussaud, J.-M. Bassat, G. Villeneuve, M. Duttine, M. Ménétrier, E. Reny, *Solid State Sci.* **2004**, *6*, 393–400.
[7] A. M. Guloy, R. Ramlau, Z. Tang, W. Schnelle, M. Baitinger, Y. Grin, *Nature* **2006**, *443*, 320–323.
[8] T. F. Fässler, *Angew. Chem. Int. Ed.* **2007**, *46*, 2572–2575.
[9] H. Kleinke, *Chem. Mater.* **2009**, *22*, 604–611.
[10] M. Christensen, S. Johnsen, B. B. Iversen, *Dalton Trans.* **2010**, *39*, 978–992.
[11] V. Pacheco, H. Gorlitz, M. Wagner-Reetz, D. Kasinathan, R. Cardoso-Gil, W. Carrillo-Cabrera, K. Meier-Kirchner, H. Rosner, Y. Grin, *Phys. Status Solidi A* **2016**, *213*, 774–783.
[12] G. A. Slack, in *CRC Handbook of Thermoelectrics* (Ed.: D. M. Rowe), CRC Press, Boca Raton, FL, **1995**, p. 407–440.
[13] Y. He, F. Sui, S. M. Kauzlarich, G. Galli, *Energ. Environ. Sci.* **2014**, *7*, 2598–2602.
[14] S. Ponou, S.-J. Kim, T. F. Fässler, *J. Am. Chem. Soc.* **2009**, *131*, 10246–10252.
[15] S.-J. Kim, Dissertation Thesis, Technische Universität München (Garching), **2007**.
[16] Q. Xie, Dissertation Thesis, Eidgenössische Technische Hochschule Zürich (Zürich), **2004**.
[17] V. Baran, A. Fischer, W. Scherer, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2013**, *639*, 2125–2128.
[18] B. M. Leu, M. I. Sturza, J. Hong, A. Alatas, V. Baran, T. F. Fässler, *EPL* **2016**, *113*, 16001.
[19] M. C. Schäfer, S. Bobev, *Chem. Mater.* **2013**, *25*, 3737–3744.
[20] G. S. Nolas, J. L. Cohn, J. S. Dyck, C. Uher, J. Yang, *Phys. Rev. B* **2002**, *65*, 165201.
[21] G. S. Nolas, T. J. R. Weakley, J. L. Cohn, *Chem. Mater.* **1999**, *11*, 2470–2473.
[22] A. P. Wilkinson, C. Lind, R. A. Young, S. D. Shastri, P. L. Lee, G. S. Nolas, *Chem. Mater.* **2002**, *14*, 1300–1305.
[23] A. Kaltzoglou, S. Ponou, T. F. Fässler, *Eur. J. Inorg. Chem.* **2008**, 4507–4510.
[24] A. Kaltzoglou, S. Ponou, T. F. Fässler, *Eur. J. Inorg. Chem.* **2008**, 538–542.
[25] V. Baran, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2015**, *641*, 1435–1443.

[26] B. Kuhl, A. Czybulka, H.-U. Schuster, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1–6.

[27] H. Zhang, G. Mu, F. Huang, X. Xie, *J. Solid State Chem.* **2016**, *242*, 155–161.

[28] W. Westerhaus, H.-U. Schuster, *Z. Naturforsch. B* **1977**, *32*, 1365–1367.

[29] Y. Liang, B. Böhme, A. Ormeci, H. Borrmann, O. Pecher, F. Haarmann, W. Schnelle, M. Baitinger, Y. Grin, *Chem. Eur. J.* **2012**, *18*, 9818–9822.

[30] Y. Liang, W. Carrillo-Cabrera, A. Ormeci, B. Bohme, M. Baitinger, Y. Grin, *Z. Anorg. Allg. Chem.* **2015**, *641*, 339–347.

[31] Y. Liang, W. Schnelle, I. Veremchuk, B. Böhme, M. Baitinger, Y. Grin, *J. Electron Mater.* **2015**, *44*, 4444–4451.

[32] K. Kishimoto, Y. Sasaki, T. Koyanagi, K. Ohoyama, K. Akai, *J. Appl. Phys.* **2012**, *111*, 093716.

[33] *WinXPOW*, Version 2.08 ed., STOE & Cie GmbH, Darmstadt, **2003**.

[34] *XPREP*, Version 6.14 ed., Bruker Nonius, **2003**.

[35] G. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

[36] G. M. Sheldrick, *SHELXS-2014: Program for the Determination of Crystal Structure*, University of Göttingen, Göttingen, Germany, **2014**.

[37] G. M. Sheldrick, *Acta Crystallogr., Sect. C* **2015**, *71*, 3–8.

[38] G. M. Sheldrick, *SHELXL-2014: Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, **2014**.

[39] S. Yamanaka, M. Komatsu, M. Tanaka, H. Sawa, K. Inumaru, *J. Am. Chem. Soc.* **2014**, *136*, 7717–7725.

[40] B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.* **2008**, 2832–2838.

[41] N. Melnychenko-Koblyuk, A. Grytsiv, L. Fornasari, H. Kaldarar, H. Michor, F. Rohrbacher, M. Koza, E. Royanian, E. Bauer, P. Rogl, M. Rotter, H. Schmid, F. Marabelli, A. Devishvili, M. Doerr, G. Giester, *J. Phys., Condens. Matter* **2007**, *19*, 216223.

www.zaac.wiley-vch.de   **7**