

# Diversity of Strontium Nitridogermanates(IV): Novel $\text{Sr}_4[\text{GeN}_4]$ , $\text{Sr}_8\text{Ge}_2[\text{GeN}_4]$ , and $\text{Sr}_{17}\text{Ge}_2[\text{GeN}_3]_2[\text{GeN}_4]_2$

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

**Abstract.** Single crystals of three new strontium nitridogermanates(IV) were grown in sealed niobium ampules from sodium flux. Dark red  $\text{Sr}_4[\text{GeN}_4]$  crystallizes in space group  $P2_1/c$  with  $a = 9.7923(2)$  Å,  $b = 6.3990(1)$  Å,  $c = 11.6924(3)$  Å and  $\beta = 115.966(1)^\circ$ . Black  $\text{Sr}_8\text{Ge}_2[\text{GeN}_4]$  contains  $\text{Ge}^{4-}$  anions coexisting with  $[\text{Ge}^{\text{IV}}\text{N}_4]^{8-}$  tetrahedra and adopts space group  $Cc$  with  $a = 10.1117(4)$  Å,  $b =$

$17.1073(7)$  Å,  $c = 10.0473(4)$  Å and  $\beta = 115.966(1)^\circ$ . Black  $\text{Sr}_{17}\text{Ge}_2\text{N}_{14}$  features the same anions alongside trigonal planar  $[\text{Ge}^{\text{IV}}\text{N}_3]^{5-}$  units. It crystallizes in  $P\bar{1}$  with  $a = 7.5392(1)$  Å,  $b = 9.7502(2)$  Å,  $c = 11.6761(2)$  Å,  $\alpha = 103.308(1)^\circ$ ,  $\beta = 94.651(1)^\circ$  and  $\gamma = 110.248(1)^\circ$ .

## Introduction

Nitridogermanates are a class of inorganic salts, most of which feature either bent  $[\text{Ge}^{\text{II}}\text{N}_2]^{4-}$  units as present in  $\text{Ca}_2[\text{GeN}_2]$  or  $[\text{Ge}^{\text{IV}}\text{N}_4]^{8-}$  tetrahedra, which were found as mutually isolated units in  $\text{Ca}_4[\text{GeN}_4]$ .<sup>[1]</sup> These latter tetrahedra may condense via edge-sharing to afford  $[\text{Ge}^{\text{IV}}_2\text{N}_6]^{10-}$  units such as in  $\text{Sr}_5[\text{Ge}_2\text{N}_6]$  or via corner-sharing, leading to infinite chains such as in  $\text{Ca}_5(\text{Ge}_2\text{N}_6)$ , or even three-dimensional networks such as in  $\text{Ca}(\text{GeN}_2)$ .<sup>[1–3]</sup> Trigonal planar  $[\text{Ge}^{\text{IV}}\text{N}_3]^{5-}$  anions appear to be less common building blocks and were so far only reported for  $\text{Ba}_9[\text{GeN}_3]_3\text{N}$ .<sup>[4]</sup> The analogous nitridosilicates are often cited as promising phosphor materials when doped appropriately.<sup>[5,6]</sup> In contrast to nitridogermanates, they have a strong tendency towards condensed networks of  $\text{SiN}_4$  tetrahedra. These tetrahedra are rarely found separated from each other, with  $\text{Ca}_4[\text{SiN}_4]$ ,<sup>[7]</sup>  $\text{Ca}_8\text{In}_2[\text{SiN}_4]$ <sup>[8]</sup> and arguably  $M(\text{Mg}_3\text{SiN}_4)$  ( $M = \text{Ca}, \text{Sr}, \text{Eu}$ )<sup>[9]</sup> being the exceptions among a plethora of condensed nitridosilicates.<sup>[6]</sup> To the best of our knowledge, neither  $[\text{Si}^{\text{II}}\text{N}_2]^{4-}$  nor  $[\text{Si}^{\text{IV}}\text{N}_3]^{5-}$  units have been reported so far.

Cations, which have been reported to form nitridogermanate salts can be divided into two groups: The larger alkaline earth metal ions calcium, strontium, and barium are typically coordinated by five or more nitrogen atoms. In contrast, smaller cat-

ions such as lithium, magnesium and 3d transition metals are typically coordinated tetrahedrally. These smaller cations may share a crystallographic site with germanium(IV) atoms, for example in the nitridogermanates  $\text{BaMg}_3\text{GeN}_4$  and  $\text{Ca}_5\text{Mg}_4\text{Ge}_3\text{N}_{10}$ .<sup>[10]</sup> The semiconductor material  $\text{ZnGeN}_2$  has been reported in an early publication to crystallize in the Wurtzite structure type with full Zn/Ge disorder,<sup>[11]</sup> but was shown to be able to adopt an ordered  $\beta\text{-NaFeO}_2$ -type Wurtzite-superstructure.<sup>[12]</sup>

Nitridogermanates(II) have been found to form mixed-anion compounds containing infinite chain Zintl-ions  $\text{Ge}^{2-}$  in  $M_3\text{Ge}[\text{GeN}_2]$  and  $M_6\text{Ge}_4[\text{GeN}_2]$  ( $M = \text{Sr}, \text{Ba}$ ).<sup>[13,14]</sup> The only instance of a nitridogermanate(II) coexisting with  $\text{Ge}^{4-}$  anions has been reported for  $\text{Sr}_{11}\text{Ge}_2[\text{GeN}_2]_2\text{N}_2$ .<sup>[15]</sup> Herein we present the first nitridogermanates(IV) containing  $\text{Ge}^{4-}$  anions, which, to the best of our knowledge, are the first inorganic compounds featuring germanium coexisting in both its highest and lowest oxidation states, +4 and –4, in one compound. We also report on the synthesis and crystal structure of the pure nitridogermanate(IV)  $\text{Sr}_4[\text{GeN}_4]$ , which crystallizes isostructural to  $\text{Ca}_4[\text{GeN}_4]$  and  $\text{Ca}_4[\text{SiN}_4]$  in the  $\text{Cs}_4[\text{PbO}_4]$  type.<sup>[1,7,16]</sup>

## Results and Discussion

Table 1 lists the most basic information about the crystal structures of the title compounds and their refinement. Further data, including atomic coordinates, displacement parameters and interatomic distances, is listed in the Supporting Information.

### $\text{Sr}_4[\text{GeN}_4]$

$\text{Sr}_4[\text{GeN}_4]$  was obtained as plate-shaped, deep red, almost black single crystals with dimensions of about 1 mm. The color is peculiar, as one would expect transparency and a lighter color from comparison with similar compounds, such as

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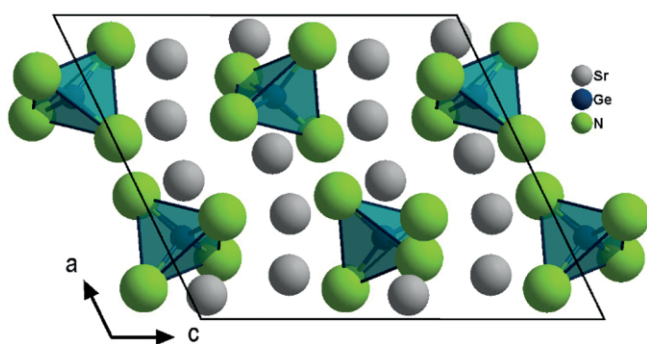
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**Table 1.** Selected crystallographic data for the title compounds.

Compound	Sr <sub>4</sub> [GeN <sub>4</sub> ]	Sr <sub>8</sub> Ge <sub>2</sub> [GeN <sub>4</sub> ]	Sr <sub>17</sub> Ge <sub>6</sub> N <sub>14</sub>
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>Cc</i>	<i>P</i> $\bar{1}$
<i>a</i> / Å	9.7923(2)	10.1117(4)	7.5392(1)
<i>b</i> / Å	6.3990(1)	17.1073(7)	9.7502(2)
<i>c</i> / Å	11.6924(3)	10.0473(3)	11.6761(2)
<i>a</i> / °	90	90	103.308(1)
<i>β</i> / °	115.966(1)	117.933(2)	94.651(1)
<i>γ</i> / °	90	90	110.248(1)
<i>R</i> <sub>int</sub> / <i>R</i> <sub>σ</sub>	0.058 / 0.019	0.122 / 0.073	0.083 / 0.027
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub>	0.019 / 0.044	0.041 / 0.085	0.029 / 0.062
GooF	1.067	1.020	1.043
<i>x</i> <sub>Flack</sub>	–	0.02(2)	–

Ca<sub>4</sub>[GeN<sub>4</sub>] (orange),<sup>[11]</sup> Sr<sub>5</sub>[Ge<sub>2</sub>N<sub>6</sub>] (yellow),<sup>[3]</sup> or Sr<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> (light red).<sup>[17]</sup> The darker color of Sr<sub>4</sub>[GeN<sub>4</sub>] does not seem to arise from surface impurities, as the fragments of crushed crystals are not noticeably lighter.

The crystal structure of Sr<sub>4</sub>[GeN<sub>4</sub>] is depicted in Figure 1. It contains mutually isolated [Ge<sup>IV</sup>N<sub>4</sub>]<sup>8-</sup> tetrahedra as exclusively occurring anions. They are oriented in four different ways according to the space group symmetry. On average, the Ge–N bonds in Sr<sub>4</sub>[GeN<sub>4</sub>] have a length of 1.93 Å, which is slightly longer than found for the other title compounds or reported elsewhere for such isolated [Ge<sup>IV</sup>N<sub>4</sub>]<sup>8-</sup> tetrahedra, for example in Ca<sub>4</sub>[GeN<sub>4</sub>] (1.91 Å),<sup>[11]</sup> Ca<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> (1.89 Å),<sup>[17]</sup> Sr<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> (1.92 Å),<sup>[17]</sup> Sr<sub>8</sub>Ge<sub>2</sub>[GeN<sub>4</sub>] (1.89 Å), and Sr<sub>17</sub>Ge<sub>6</sub>N<sub>14</sub> (1.90 Å in tetrahedra). The Ge(1)–N(3) distance in Sr<sub>4</sub>[GeN<sub>4</sub>] amounts to 2.00 Å, making it the longest Ge–N bond reported in an orthonitridogermanate(IV), with the isostructural Ca<sub>4</sub>[GeN<sub>4</sub>] coming closest at 1.95 Å.<sup>[11]</sup> When compared to Ca<sub>4</sub>[GeN<sub>4</sub>], the larger tetrahedra in Sr<sub>4</sub>[GeN<sub>4</sub>] can be explained with the larger space provided by the matrix of strontium atoms. Similar trends are observed in many other compounds, including the aforementioned Ca<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> and Sr<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub>.<sup>[17]</sup>

**Figure 1.** Extended unit cell of Sr<sub>4</sub>[GeN<sub>4</sub>] highlighting mutually isolated tetrahedra [GeN<sub>4</sub>]<sup>8-</sup>.

Strontium atoms are coordinated by five or six nitrogen atoms each, with each individual [Ge<sup>IV</sup>N<sub>4</sub>]<sup>8-</sup> tetrahedron contributing up to two nitrogen atoms. The coordination polyhedra resemble square pyramids for Sr(1) and Sr(4), a trigonal bipyramid for Sr(2) and an octahedron in the case of Sr(3). Nitrogen atoms are coordinated by one germanium and five or six strontium atoms each, resulting in octahedra for atoms N(1)

and N(4), a trigonal prism for N(2) and a capped trigonal prism for N(3), the cap being on one of the faces with a germanium corner.

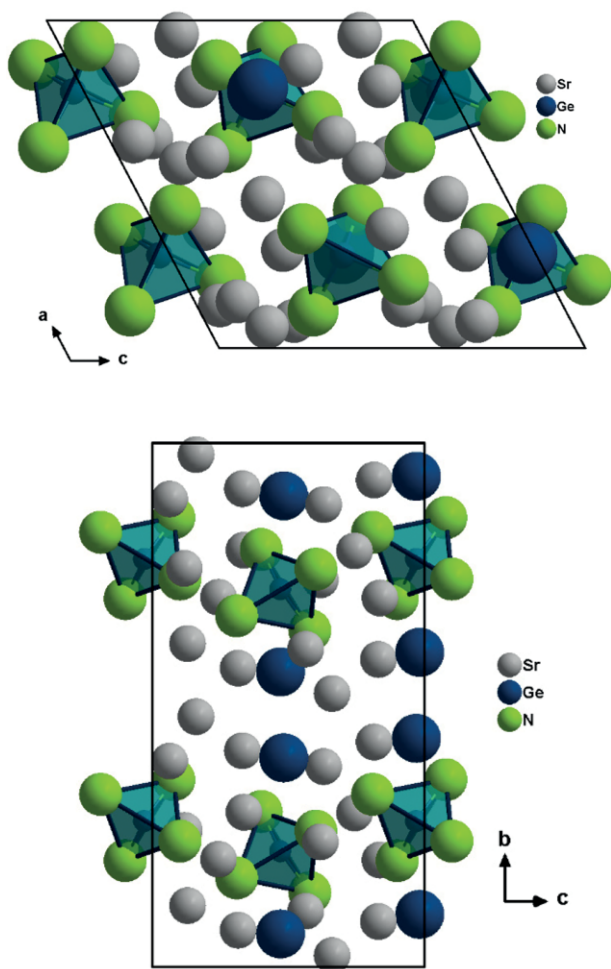
### Sr<sub>8</sub>Ge<sub>2</sub>[GeN<sub>4</sub>]

Sr<sub>8</sub>Ge<sub>2</sub>[GeN<sub>4</sub>] was obtained in the form of black, plate-shaped single crystals of up to 0.15 mm in length and width. It contains a tetrahedral [Ge<sup>IV</sup>N<sub>4</sub>]<sup>8-</sup> unit as well as two crystallographically distinct, isolated Ge<sup>4-</sup> anions. These anions form alternating layers perpendicular to *b*, as shown in Figure 2. While the average Ge–N distance in Sr<sub>8</sub>Ge<sub>2</sub>[GeN<sub>4</sub>] amounts to 1.89 Å, one of the bonds is much shorter at 1.83 Å. The surrounding of the strontium atoms is quite variable, with one to five nitrogen atoms and one to three germanide ions contributing to the coordination, resulting in overall coordination numbers ranging from 4 to 6. The tetrahedral [Ge<sup>IV</sup>N<sub>4</sub>]<sup>8-</sup> unit may coordinate in a mono-, bi-, or tridentate fashion. The nitrogen atoms N(2), N(3) and N(4) are coordinated by distorted octahedra, formed from five strontium atoms and the Ge(3) atom, the latter of which has a much shorter distance to the central nitrogen atom. The coordination polyhedron of N(1) is best described as a pentagonal bipyramid with atoms Ge(3) and Sr(4) on the apical position having the shortest distances to N(1). The equatorial positions are occupied by three strontium atoms at an intermediate distance and by two more remote strontium atoms. Each germanide ion is coordinated by ten strontium atoms in an irregular fashion, with Ge–Sr distances ranging from 3.08 to 4.40 Å.

The metric of the unit cell of Sr<sub>8</sub>Ge<sub>2</sub>[GeN<sub>4</sub>] (see Table 1) is quite close to a hexagonal or trigonal cell. However, the actual crystal structure does not seem to support any such relation, leaving coincidence as the best explanation. The non-centric space group *Cc* may also appear suspicious, but the more common space group *C2/c* can be ruled out by considering both the lack of an inversion center in the crystal structure (see Figure 2) and the Flack parameter ranging within a standard deviation of zero.

### Sr<sub>17</sub>Ge<sub>6</sub>N<sub>14</sub>

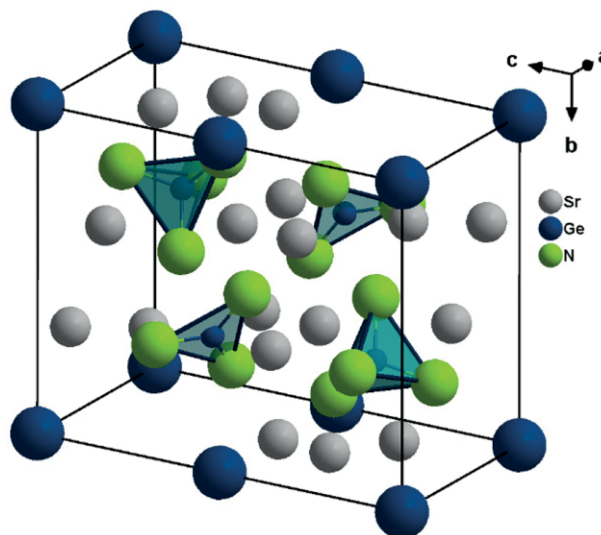
Sr<sub>17</sub>Ge<sub>6</sub>N<sub>14</sub> = Sr<sub>17</sub>Ge<sub>2</sub>[GeN<sub>3</sub>]<sub>2</sub>[GeN<sub>4</sub>]<sub>2</sub> was obtained in the form of black, prolate, irregularly shaped single crystals, which



**Figure 2.** Extended unit cell of  $\text{Sr}_3\text{Ge}_2[\text{GeN}_4]$  viewed along  $b$  (top) and  $a$  (bottom). The representations of germanide ions are displayed larger than those of  $\text{Ge}^{\text{IV}}$  atoms.

measure up to 0.1 mm in length. Its unit cell, as depicted in Figure 3, contains two crystallographically equivalent trigonal planar  $[\text{Ge}^{\text{IV}}\text{N}_3]^{5-}$  units and two equivalent  $[\text{Ge}^{\text{IV}}\text{N}_4]^{8-}$  tetrahedra, as well as two distinct  $\text{Ge}^{4+}$  anions. The Ge–N distances in the  $[\text{Ge}^{\text{IV}}\text{N}_4]^{8-}$  tetrahedra range between 1.88 and 1.92 Å, which fits well with such mutually isolated tetrahedra in other compounds as discussed in the  $\text{Sr}_4[\text{GeN}_4]$  section. The distances in the  $[\text{Ge}^{\text{IV}}\text{N}_3]^{5-}$  unit on average amount to 1.80 Å, which is close to the 1.79 Å reported for  $\text{Ba}_9[\text{GeN}_3]_3\text{N}$ ,<sup>[4]</sup> the only other compound known to contain these units. The shorter bond length compared to the tetrahedra can probably be attributed to both the lower coordination number and partial  $\pi$ -bonding contributions.

Strontium atoms are irregularly coordinated by three to six nitrogen atoms and up to two  $\text{Ge}^{4+}$  anions, resulting in overall coordination numbers ranging from 5 to 7. Each  $[\text{Ge}^{\text{IV}}\text{N}_3]^{5-}$  unit may contribute up to two and each  $[\text{Ge}^{\text{IV}}\text{N}_4]^{8-}$  tetrahedron up to three nitrogen atoms to the environment of a given strontium atom. The coordination polyhedra of nitrogen atoms N(1), N(2), N(3), N(5) and N(6) are best described as distorted octahedra, each with five coordinating strontium atoms and a

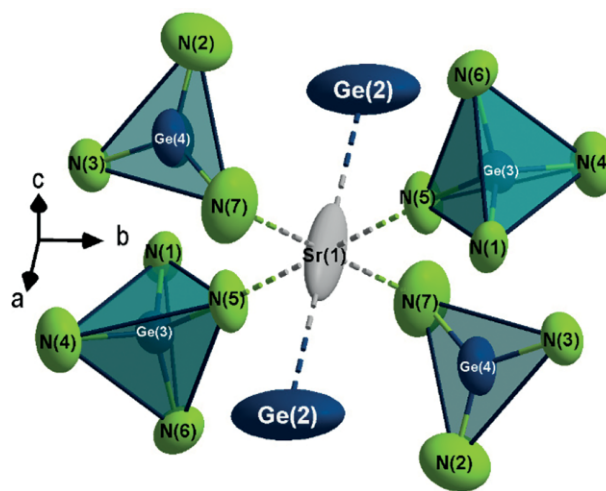


**Figure 3.** Unit cell of  $\text{Sr}_{17}\text{Ge}_6\text{N}_{14}$ . The representations of germanide ions are displayed larger than those of  $\text{Ge}^{\text{IV}}$  atoms.

shorter bond to either Ge(3) or Ge(4). The strontium atom on the side opposite to the Ge–N bond consistently has the shortest Sr–N distance. Atoms N(4) and N(7) are each coordinated by distorted, capped trigonal prisms constructed by one germanium and six strontium atoms, with the cap on one of the tetragonal faces containing the germanium atom.

Germanide ions are coordinated roughly cuboctahedrally by strontium atoms. However, the coordination polyhedron of Ge(1) may as well be described as a four-capped cuboid, with the four more remote strontium atoms having an average Ge–Sr distance of 4.13 Å while the eight closer ones are on average only 3.43 Å away.

Suspiciously high displacement parameters are found for atoms Sr(1) and Ge(2). For Sr(1), the displacement ellipsoid is strongly elongated along  $a$ , as depicted in Figure 4. This appears to be due to a rather peculiar tetragonal planar coordina-



**Figure 4.** Coordination environment of the Sr(1) atom in  $\text{Sr}_{17}\text{Ge}_6\text{N}_{14}$  with the atoms represented by their displacement ellipsoids at 95% probability.

tion by four nitrogen atoms. The distance to the two closest nitrogen atoms is rather short at 2.42 Å each, while there is ample space along the *a* axis, where the closest neighbors are two germanide ions, each with a distance of 3.77 Å. In refinements the occupation parameter does not significantly deviate from full occupation [0.504(3)], and the shape and extension of the displacement ellipsoid persist even upon symmetry reduction to *P*1. This leads to the question if Sr(1) actually occupies the *1f* site or rather a split position with perpendicular displacement along *a*. Refinement of the single crystal diffraction data collected at room temperature with a split position at 50% occupation yields a distance of 0.50 Å between the resulting positions. However, introducing this split position does not significantly improve the quality of the refinement ( $wR_2 = 0.062$ , GooF = 1.041, compare Table 1).

The displacement ellipsoid of Ge(2) is more spherical than that of Sr(1), but unusually large nonetheless. Reasons for this might include its coordination polyhedron which appears to be slightly too large for a Ge<sup>4+</sup> ion. This becomes evident when comparing the Ge–Sr distances of Ge(1) and Ge(2), which are on average 0.06 Å longer for Ge(2). The difference is exacerbated when only looking at the eight closest neighbors. Those are on average 0.19 Å further away than the eight closest neighbors of Ge(1). The misbehaved Sr(1) atom contributing to the coordination might also enlarge the displacement ellipsoid of Ge(2). A refined site occupation factor again did not significantly deviate from full occupation [0.500(4)].

## Conclusions

Single crystals of three new nitridogermanates were grown from sodium flux. They share mutually isolated [Ge<sup>IV</sup>N<sub>4</sub>]<sup>8-</sup> tetrahedra as one of their structural features. Sr<sub>4</sub>[GeN<sub>4</sub>] is the most simple strontium orthonitridogermanate(IV) and is isostructural to Ca<sub>4</sub>[GeN<sub>4</sub>] and Ca<sub>4</sub>[SiN<sub>4</sub>]. Sr<sub>17</sub>Ge<sub>6</sub>N<sub>14</sub> and Sr<sub>8</sub>Ge<sub>2</sub>[GeN<sub>4</sub>] share an unprecedented combination of Ge<sup>4+</sup> Zintl-anions and [Ge<sup>IV</sup>N<sub>4</sub>]<sup>8-</sup> tetrahedra, with Sr<sub>17</sub>Ge<sub>6</sub>N<sub>14</sub> also featuring the rarely seen trigonal planar [Ge<sup>IV</sup>N<sub>3</sub>]<sup>5-</sup> units. These compounds underline the flexibility of the nitride chemistry of germanium, in contrast to that of silicon, where neither [Si<sup>IV</sup>N<sub>3</sub>]<sup>5-</sup> units nor coexisting Si<sup>4+</sup> ions have been reported as of yet. They also confirm the tendency of nitridogermanates to form mutually isolated units, as opposed to the typically heavily condensed nitridosilicates.

## Experimental Section

Since both starting materials and products are highly sensitive to oxygen and moisture, all manipulations were carried out in a glovebox in an argon atmosphere (MBraun, ≤ 1 ppm O<sub>2</sub>). Strontium nitride Sr<sub>2</sub>N was prepared by placing a tantalum crucible with strontium metal (dentritic, Sigma–Aldrich, 99.99%) in a quartz tube and heating for 8 h at 550 °C in nitrogen atmosphere (Alphagaz, 99.999%). The product was crushed and re-reacted for another 8 h.

Single crystals of Sr<sub>4</sub>[GeN<sub>4</sub>] and Sr<sub>17</sub>Ge<sub>6</sub>N<sub>14</sub> were grown from strontium nitride, germanium nitride, Ge<sub>3</sub>N<sub>4</sub>, and sodium azide NaN<sub>3</sub> in molar ratios of 9:2:3, while those of Sr<sub>8</sub>Ge<sub>2</sub>[GeN<sub>4</sub>] resulted from mix-

tures of strontium nitride and germanium in the molar ratio 6:5. In all cases, sodium metal was added as flux. The reactions took place in sealed niobium ampules, which were put in a steel crucible and heated to 720 °C inside a quartz tube under argon for 72 h, after which they were allowed to naturally cool to room temperature. Sodium was removed by extraction with liquid ammonia. These syntheses typically resulted in a variety of products, often including the strontium nitridogermanates Sr<sub>2</sub>[GeN<sub>2</sub>], Sr<sub>5</sub>[Ge<sub>2</sub>N<sub>6</sub>] and Sr<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> alongside the title compounds.<sup>[3,14,17]</sup> Single crystals with well-defined features were selected and sealed in glass capillaries. X-ray diffraction data was collected on a Bruker κ-CCD single crystal diffractometer using Mo-*K*<sub>α</sub> radiation. A numerical absorption correction was applied using X-SHAPE and the structure model was solved and refined using the SHELX software.<sup>[18]</sup> Graphical representations of the structure were created in Diamond.<sup>[19]</sup> Selected information on the structure determinations, atomic parameters and selected interatomic distances are listed in Tables S1–S10 (Supporting Information).

Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, <http://www.fiz-karlsruhe.de/request-for-deposited-data.html>) on quoting the depository numbers CSD-1972763 (Sr<sub>4</sub>[GeN<sub>4</sub>]), CSD-1972762 (Sr<sub>8</sub>Ge<sub>2</sub>[GeN<sub>4</sub>]), and CSD-1972761 (Sr<sub>17</sub>Ge<sub>6</sub>N<sub>14</sub>).

**Supporting Information** (see footnote on the first page of this article): Details on crystal structure determinations and refinements.

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**Keywords:** Nitrides; Nitridogermanates; Sodium flux; Germanium; Zintl anions

## References

- [1] S. J. Clarke, F. J. DiSalvo, *Inorg. Chem.* **2000**, *39*, 2631–2634.
- [2] M. Maunaye, J. Guyader, Y. Laurent, J. Lang, *Bull. Soc. Fr. Minéral. Cristallogr.* **1971**, *94*, 347–352.
- [3] S. C. Junggeburth, O. Oeckler, W. Schnick, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1309–1311.
- [4] D. G. Park, F. J. DiSalvo, *Bull. Korean Chem. Soc.* **2008**, *29*, 2413–2418.
- [5] R.-J. Xie, N. Hirosaki, Y. Li, T. Takeda, *Materials* **2010**, *3*, 3777–3793.
- [6] M. Zeuner, S. Pagano, W. Schnick, *Angew. Chem. Int. Ed.* **2011**, *50*, 7754–7775.
- [7] H. Yamane, H. Morito, *Inorg. Chem.* **2013**, *52*, 5559–5563.
- [8] M. J. Dickman, B. V. G. Schwartz, S. E. Lattner, *Inorg. Chem.* **2017**, *56*, 9361–9368.
- [9] S. Schmiechen, H. Schneider, P. Wagatha, C. Hecht, P. J. Schmidt, W. Schnick, *Chem. Mater.* **2014**, *26*, 2712–2719.
- [10] a) C. Poesl, R. Niklaus, W. Schnick, *Eur. J. Inorg. Chem.* **2017**, *2017*, 2422–2427; b) C. Poesl, W. Schnick, *Eur. J. Inorg. Chem.* **2017**, *2017*, 1498–1503.

- [11] W. L. Larson, H. P. Maruska, D. A. Stevenson, *J. Electrochem. Soc.* **1974**, *121*, 1673.
- [12] M. Wintenberger, M. Maunaye, Y. Laurent, *Mater. Res. Bull.* **1973**, *8*, 1049–1053.
- [13] D. G. Park, F. J. DiSalvo, *Bull. Korean Chem. Soc.* **2005**, *26*, 1543–1548.
- [14] S. J. Clarke, G. R. Kowach, F. J. DiSalvo, *Inorg. Chem.* **1996**, *35*, 7009–7012.
- [15] Z. A. Gál, S. J. Clarke, *Chem. Commun.* **2005**, 728–730.
- [16] U. Müller, K. Bernet, R. Hoppe, *Z. Anorg. Allg. Chem.* **1992**, *612*, 143–148.
- [17] S. C. Junggeburth, O. Oeckler, D. Johrendt, W. Schnick, *Inorg. Chem.* **2008**, *47*, 12018–12023.
- [18] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
- [19] H. Putz, K. Brandenburg, *Diamond, Bonn* **2014**.

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