

## Nitridogermanate Nitrides $\text{Sr}_7[\text{GeN}_4]\text{N}_2$ and $\text{Ca}_7[\text{GeN}_4]\text{N}_2$ : Synthesis Employing Sodium Melts, Crystal Structure, and Density-Functional Theory Calculations

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The alkaline earth nitridogermanate nitrides  $\text{AE}_7[\text{GeN}_4]\text{N}_2$  ( $\text{AE} = \text{Ca}, \text{Sr}$ ) have been synthesized using a Na flux technique in sealed Ta tubes. According to single-crystal X-ray diffraction the isotopic compounds crystallize in space group *Pbcn* (No. 60) with  $Z = 4$ , ( $\text{Sr}_7[\text{GeN}_4]\text{N}_2$ :  $a = 1152.6(2)$ ,  $b = 658.66(13)$ ,  $c = 1383.6(3)$  pm,  $V = 1050.5(4) \times 10^6$  pm<sup>3</sup>,  $R1 = 0.049$ ;  $\text{Ca}_7[\text{GeN}_4]\text{N}_2$ :  $a = 1082.6(2)$ ,  $b = 619.40(12)$ ,  $c = 1312.1(3)$  pm,  $V = 879.8(3) \times 10^6$  pm<sup>3</sup>,  $R1 = 0.016$ ). Owing to the high N/Ge ratio, the compounds contain discrete  $\text{N}^{3-}$  ions coordinated by six  $\text{AE}^{2+}$  besides discrete  $[\text{GeN}_4]^{8-}$  tetrahedrons. One of the  $\text{AE}^{2+}$  ion is coordinated by only four  $\text{N}^{3-}$  ions, which is rather an unusual low coordination number for  $\text{Sr}^{2+}$ . Together with the isolated  $[\text{GeN}_4]^{8-}$  tetrahedrons, these  $\text{Sr}^{2+}$  ions form chains of alternating cation centered edge sharing tetrahedrons. The electronic structure and chemical bonding in  $\text{Sr}_7[\text{GeN}_4]\text{N}_2$  has been analyzed employing linear muffin-tin orbital (LMTO) band structure calculations.

### Introduction

In the last years the interest in the preparation of new ternary germanium nitrides has seen rapid growth because of their interesting structural chemistry.<sup>1–6</sup> A new way to synthesize these compounds with the aid of sodium melts has been established by DiSalvo et al.<sup>6</sup> Single nitridogermanate crystals containing the alkaline earth elements Ca, Sr, and Ba and sometimes additional Li have been grown in liquid Na as a flux under a  $\text{N}_2$  pressure in situ generated by the decomposition of  $\text{NaN}_3$  in sealed tubes. The alkaline earth metals may increase the solubility of nitrogen in liquid Na.<sup>7,8</sup>

There are a number of nitridosilicates containing highly condensed networks of  $\text{SiN}_4$  tetrahedrons, which are stable

when exposed to air.<sup>9</sup> In contrast, the synthesis and characterization of nitridogermanates is more challenging, especially if their degree of condensation of the tetrahedral units is low. It has been shown that highly condensed tetrahedral networks are kinetically inert and do not hydrolyze to form the thermodynamically stable oxo-compound. In contrast to silicon the heavier homologue germanium can also form anionic  $\text{GeN}_2^{4-}$  units with Ge(II) (e.g., in  $\text{Sr}_2\text{GeN}_2$ ).<sup>3</sup>

In solid-state compounds,  $\text{Sr}^{2+}$  usually exhibits coordination number of five or higher; to our knowledge there are only few examples of  $\text{Sr}^{2+}$  with a 4-fold coordination, for example,  $\text{Sr}_6\text{Cu}_3\text{N}_5$ <sup>10</sup> and  $\text{Sr}_2\text{FeN}_2$ .<sup>11</sup> Here, we report on the synthesis and structure determination of  $\text{Sr}_7[\text{GeN}_4]\text{N}_2$ , a new nitrogen rich nitridogermanate nitride containing  $\text{Sr}^{2+}$  ions with unusual low coordination number four.

### Experimental Section

All manipulations were carried out in an argon-filled recirculation glovebox (MBraun, Garching;  $\text{O}_2 < 1$  ppm,  $\text{H}_2\text{O} < 1$  ppm). The starting materials were Sr metal (ABCR GmbH Co. KG, Karlsruhe, 99.9%), Na metal (Fluka 99%),  $\text{NaN}_3$  (Acros, 99%), elemental Ge

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**Table 1.** Crystal Data and Refinement Details of 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>a</sup>

Compound	Ca <sub>7</sub> [GeN <sub>4</sub> ]N <sub>2</sub>	Sr <sub>7</sub> [GeN <sub>4</sub> ]N <sub>2</sub>
formula mass/g mol <sup>-1</sup>	437.18	769.97
temperature/ K	200(2)	293(2)
crystal system		orthorhombic
space group		<i>Pbcn</i> (No. 60)
cell parameters/pm	<i>a</i> = 1082.6(2) <i>b</i> = 619.40(12) <i>c</i> = 1312.1(3)	<i>a</i> = 1152.6(2) <i>b</i> = 658.66(13) <i>c</i> = 1383.6(3)
cell volume/10 <sup>6</sup> pm <sup>3</sup>	879.8(3)	1050.5(4)
formula units/cell		4
crystal shape, color	platelet, yellow	block, red
crystal size/mm <sup>3</sup>	0.14 × 0.06 × 0.03	0.15 × 0.10 × 0.07
X-ray density/g cm <sup>-3</sup>	3.301	4.869
abs. coefficient μ/mm <sup>-1</sup>	7.514	38.040
<i>F</i> (000)	856	1360
diffractometer	Nonius Kappa CCD	Stoe IPDS
radiation		Mo Kα, (λ = 71.073 pm)
absorption correction	semiempirical <sup>15</sup>	numerical <sup>14</sup>
θ range/deg	3.6–27.6	2.3–30.4
measured reflections	15719	9888
independent reflections	1012	1524
observed reflections	935	1085
refined parameters	66	66
GOF	1.082	0.916
<i>R</i> indices ( <i>F</i> <sub>o</sub> <sup>2</sup> ≥ 2σ( <i>F</i> <sub>o</sub> <sup>2</sup> ))	<i>R</i> 1 = 0.0135, <i>wR</i> 2 = 0.0293	<i>R</i> 1 = 0.0265, <i>wR</i> 2 = 0.0505
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0162, <i>wR</i> 2 = 0.0304	<i>R</i> 1 = 0.0492, <i>wR</i> 2 = 0.0543
max./min residual electron density/ e Å <sup>-3</sup>	–0.358/0.321	–0.991/0.261

<sup>a</sup> e.s.d.'s in parentheses.

(Smart Elements, 99.9999%), Ca metal (Alfa Aesar, 99.98%) and GeO<sub>2</sub> (Aldrich, 99.998%). Ta crucibles (wall thickness 0.5 mm, internal diameter 1 cm) were cleaned in a mixture of HNO<sub>3</sub> (conc.) and HF (40%). Initially, we have utilized GeO<sub>2</sub> as a starting material because we have targeted the synthesis of new oxonitridogermanates. However, in the Na flux apparently GeO<sub>2</sub> has been fully reduced leading to nitridic products. For the synthesis of Sr<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub>, 58.1 mg (0.90 mmol) NaN<sub>3</sub>, 27.0 mg (0.26 mmol) GeO<sub>2</sub>, 113.7 mg (1.30 mmol) Sr, and 127.3 mg (5.54 mmol) Na were placed into the crucible before it was sealed under a pressure of 1 bar purified Ar in an arc furnace. The crucible holder was water-cooled and when sealing the crucible, care was taken to avoid the decomposition of NaN<sub>3</sub> at approximately 300 °C. The sealed crucible was transferred into a silica glass tube under vacuum to prevent oxidation and then it was placed into a tube furnace. The furnace was heated to 760 °C with a rate of about 60 °C/h, maintained for 48 h, cooled to 300 °C with a rate of about 3 °C/h. Finally, the furnace was switched off. The tube was opened in a glovebox and transferred into a flow-tube furnace using Schlenk techniques. Excess sodium was removed under a dynamic vacuum at 320 °C within 3 h. The crystals were transferred into a Schlenk tube under argon atmosphere. The product consists of a black powder containing two types of crystals. Besides orange ones which could be identified as Sr<sub>5</sub>Ge<sub>2</sub>N<sub>6</sub>,<sup>12</sup> red single crystals of the title compound were obtained.

Ca<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> was synthesized by an analogous procedure but elementary Ge instead of GeO<sub>2</sub> was used. The following starting materials were employed: 501.7 mg (21.8 mmol) Na, 22 mg (0.34 mmol) NaN<sub>3</sub>, 10 mg Ge (0.14 mmol), and 38.6 mg (0.96 mmol) Ca. The furnace was heated to 900 °C with a rate of about 120 °C/h, maintained for 24 h, cooled to 400 °C with a rate of about 3 °C/h, and subsequently the furnace was switched off. The product consists of a black powder and some single yellow crystals. When

exposed to air, both products 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> hydrolyze to a white powder under evolution of NH<sub>3</sub> indicating their nitridic character.

The determination of the metrics of single crystals was carried out using a STOE IPDS diffractometer with graphite monochromated Mo Kα radiation (71.073 pm). Intensity data were collected using a Nonius Kappa-CCD diffractometer with graded multilayer X-ray optics and a STOE IPDS diffractometer, respectively. The structures were solved by direct methods using SHELXS-97<sup>13</sup> and refined with anisotropic displacement parameters by full-matrix least-squares calculations on *F*<sup>2</sup> (SHELXL-97).<sup>13</sup> The data were numerically corrected for absorption (X-Red)<sup>14</sup> after optimizing the crystal shape with XSHAPE<sup>14</sup> and semiempirically by using the software SADABS,<sup>15</sup> respectively. The atomic parameters were standardized using the program STRUCTURE TIDY.<sup>16</sup> The approximate molar ratio Sr/Ge and Ca/Ge, respectively, was confirmed by energy dispersive X-ray analysis (JSM 6500F scanning electron microscope, Jeol; detector model 7418, Oxford Instruments).

Density-functional theory (DFT) band structure calculations were performed using the linear muffin-tin orbital (LMTO)-method in its scalar-relativistic version (program TB-LMTO-ASA).<sup>17</sup> Detailed descriptions are given elsewhere.<sup>18</sup> Reciprocal space integrations were performed with the tetrahedron method using 45 irreducible *k*-points out of 128 (grid of 4 × 8 × 4) in the Brillouin zone.<sup>19</sup> The basis set consisted of Sr-5s/(5p)/4d/(4f), Ge-4s/4p/(4d), and

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**Table 2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters (in  $10^{-4}$  pm<sup>2</sup>) for 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>a</sup>

atom	Wyckoff position	x	y	z	U <sub>eq</sub>
AE1	8d	0.03899(3)	0.26844(6)	0.47826(3)	0.00617(9)
		0.03912(4)	0.26287(9)	0.47862(3)	0.00907(12)
AE2	8d	0.22942(3)	0.14320(6)	0.12672(3)	0.00634(9)
		0.22647(4)	0.14472(8)	0.12616(3)	0.00979(12)
AE3	8d	0.29670(3)	0.39101(6)	0.38278(3)	0.00584(9)
		0.29593(4)	0.38896(8)	0.37661(3)	0.00841(11)
AE4	4c	0	0.55840(9)	1/4	0.00798(12)
		0	0.55958(12)	1/4	0.01252(15)
Ge1	4c	0	0.06689(4)	1/4	0.00420(8)
		0	0.07041(12)	1/4	0.00647(16)
N1	8d	0.13278(13)	0.2453(2)	0.29304(11)	0.0074(3)
		0.1259(4)	0.2414(7)	0.2912(2)	0.0073(8)
N2	8d	0.16664(14)	0.4063(2)	0.00553(11)	0.0072(3)
		0.1662(4)	0.4077(8)	0.0021(3)	0.0099(9)
N3	8d	0.45153(14)	0.3896(2)	0.14101(12)	0.0093(3)
		0.4541(4)	0.4007(8)	0.1436(3)	0.0131(10)

<sup>a</sup> e.s.d.'s. in parentheses. First line Ca-compound, second line Sr-compound.

N-2s/2p(3d). Orbitals given in parentheses were downfolded.<sup>20</sup> To achieve space filling within the atomic sphere approximation, interstitial spheres are introduced to avoid too large overlap of the atom-centered spheres. The COHP (crystal orbital Hamilton population)<sup>21</sup> method was used for the bond analysis. COHP gives the energy contributions of all electronic states for a selected bond. The values are negative for bonding and positive for antibonding interactions. With respect to crystal orbital overlap population (COOP) diagrams, we plot -COHP(E) to obtain positive values for bonding states.

## Results and Discussion

**Crystal Structure Determination.** The crystal structure of Sr<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> was solved by single-crystal X-ray diffraction data (cf. Table 1). Systematic extinctions indicated space group *Pbcn* (No. 60). The structure solution yielded unequivocally the positions of the Sr and Ge atoms. The positions of the N atoms were located from a difference Fourier map. The final structure refinement converged to *R*1 = 0.0492 for all data. The resulting composition Sr<sub>7</sub>GeN<sub>6</sub> agrees roughly with the molar ratio of Sr: Ge = 6.4: 1 detected by EDX analysis on single crystals.

The yellow crystals of Ca<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> are isotypic with the respective strontium compound (cf. Table 1). Lattice parameters of the Ca-compound are slightly smaller because of the smaller ionic radius of Ca<sup>2+</sup>. In the following, figures and structure descriptions focus on Sr<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> while the details of Ca<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> are not discussed separately. Crystal data and refinement details are summarized in Table 1. The atomic parameters and anisotropic displacement parameters of Sr<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> and Ca<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> are listed in Tables 2 and 3. Bond lengths in Sr<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> are listed in Table 4. For comparison, bond lengths of the Ca compound are also listed in Table 4. Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-419596 (Sr<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub>) and CSD-419592 (Ca<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub>), respectively, as well as the

names of the authors and citation of the paper (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de).

**Structure Description.** According to the formula Sr<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> there are isolated N<sup>3-</sup> ions besides non condensed [GeN<sub>4</sub>]<sup>8-</sup> tetrahedrons. The latter ones have also been found in Ca<sub>4</sub>GeN<sub>4</sub>.<sup>1</sup> Both types of anions are embedded in a matrix of Sr<sup>2+</sup> (cf. Figure 1a). Similar structural motifs are known from the structural chemistry of nitridogallates with additional discrete nitride ions coordinated by alkaline earth ions. For example, Sr<sub>3</sub>GaN<sub>3</sub> contains only isolated planar [GaN<sub>3</sub>]<sup>6-</sup> nitridogallate units surrounded by Sr<sup>2+</sup> ions, whereas in Sr<sub>6</sub>[GaN<sub>3</sub>]N<sub>2</sub> additional N<sup>3-</sup> ions coordinated by Sr<sup>2+</sup> are formally building up Sr<sub>3</sub>N<sub>2</sub> blocks.<sup>22</sup> Ca<sub>6</sub>[GaN<sub>3</sub>]N<sub>2</sub><sup>23</sup> and its transition metal analogues Sr<sub>6</sub>[MnN<sub>3</sub>]N<sub>2</sub><sup>24</sup> and Sr<sub>6</sub>[FeN<sub>3</sub>]N<sub>2</sub><sup>23</sup> are isostructural with Sr<sub>6</sub>[GaN<sub>3</sub>]N<sub>2</sub>.

The bonding distances Ge–N in Sr<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub> (192.2(4) and 192.3(5) pm) and angles N–Ge–N (∠N1–Ge–N1 108.3(3) and ∠N2–Ge–N2 108.9(3)°) are quite similar, and in the range of typical values.<sup>1,3,25</sup> In Ca<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub>, the distances Ge–N are slightly shorter than in the isotypic Sr-compound (187.8(1) and 189.9(1) pm) while the angles are nearly equal (∠N1–Ge1–N1 108.8(1)° and ∠N2–Ge–N2 108.4(1)°). Slightly different Ge–N distances in both compounds are presumably due to different measurement temperatures of the crystals.

Sr4 has a 4-fold coordination, which is rather unusual for the large Sr<sup>2+</sup>. This atom is surrounded by N<sup>3-</sup> originating of the isolated [GeN<sub>4</sub>]<sup>8-</sup> entities with distances Sr–N ranging from 261.2(5) to 273.7(5) pm (cf. Figure 1b). These bonds are considerably longer than the shortest distances Sr–N in this crystal structure (248.6(4) pm). Taking into account the different ionic radii of Sr<sup>2+</sup> and Ge<sup>4+</sup>, it seems rather improbable that there is a mixed occupancy Ge/Sr in Sr<sub>7</sub>[GeN<sub>4</sub>]N<sub>2</sub>. Accordingly, refinement of the occupancy factors gives no indication of disorder concerning the Sr<sup>2+</sup> ions. In comparison to the isotypic Ca-compound the low coordination number is here not unusual because of the smaller ionic radius of Ca<sup>2+</sup>.

Coordination number four of Sr<sup>2+</sup> has rarely been found in solid-state compounds. To our knowledge there are only a few examples, for example, Sr<sub>6</sub>Cu<sub>3</sub>N<sub>5</sub><sup>10</sup> and Sr<sub>2</sub>FeN<sub>2</sub>.<sup>11</sup> In Sr<sub>6</sub>Cu<sub>3</sub>N<sub>5</sub> the less coordinated Sr<sup>2+</sup> has three close neighbors (261–267 pm) and one distant neighbor (291 pm), while in Sr<sub>2</sub>FeN<sub>2</sub> the strontium is coordinated by N<sup>3-</sup> (254–277 pm) in a distorted tetrahedral arrangement. The same low coordination number for Sr<sup>2+</sup> was also discussed in molecular compounds like in 12-crown-4 ether complexes<sup>26</sup> and in the chemistry of Sr-gallates.<sup>27</sup> The distances of Sr<sup>2+</sup> to the next

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**Table 3.** Anisotropic Displacement Parameters (in  $10^{-4}$  pm<sup>2</sup>) for  $Ca_7[GeN_4]N_2$  (First Line) and  $Sr_7[GeN_4]N_2$  (Second Line)<sup>a</sup>

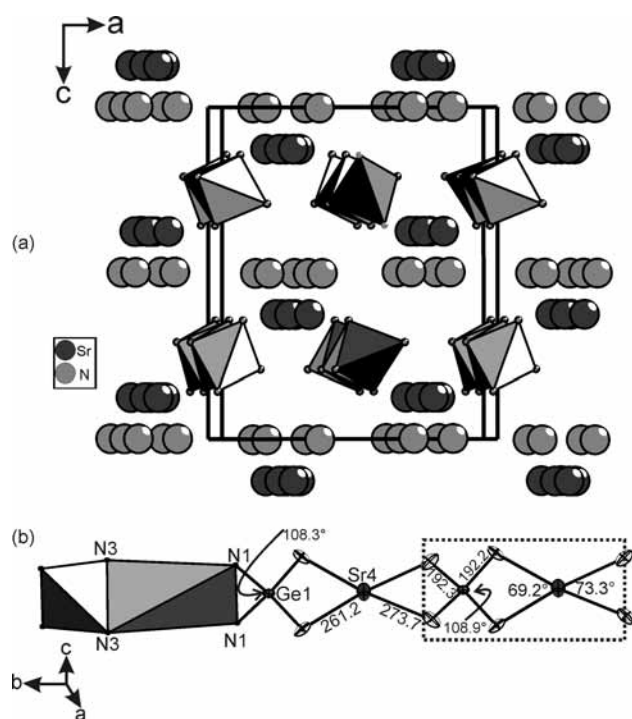
atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
AE1	0.00643(17)	0.00608(18)	0.00599(17)	0.00049(13)	0.00063(13)	0.00023(13)
	0.0090(2)	0.0101(2)	0.00816(17)	0.00024(19)	0.00100(14)	0.0002(2)
AE2	0.00716(17)	0.00649(18)	0.00537(17)	−0.00014(13)	0.00055(13)	0.00090(13)
	0.0103(2)	0.0111(2)	0.00792(18)	0.00009(18)	0.00079(15)	0.00154(18)
AE3	0.00572(17)	0.00579(18)	0.00599(17)	0.00007(13)	−0.00039(13)	−0.00071(14)
	0.0078(2)	0.0090(2)	0.00841(18)	0.00006(18)	−0.00072(15)	−0.00115(17)
AE4	0.0071(2)	0.0054(2)	0.0115(3)	0	0.00049(19)	0
	0.0105(4)	0.0088(3)	0.0182(3)	0	0.0009(2)	0
Ge1	0.00431(13)	0.00434(14)	0.00396(14)	0	−0.00029(9)	0
	0.0064(4)	0.0075(4)	0.0054(3)	0	−0.0001(2)	0
N1	0.0071(2)	0.0072(7)	0.0081(7)	−0.0012(6)	−0.0002(6)	−0.0003(6)
	0.007(2)	0.004(2)	0.0111(15)	−0.0016(17)	−0.0009(12)	−0.0009(18)
N2	0.0068(7)	0.0084(7)	0.0063(7)	0.0004(6)	0.0000(6)	0.0004(6)
	0.009(2)	0.010(3)	0.0110(16)	0.0005(16)	−0.0016(15)	0.0013(19)
N3	0.0096(7)	0.0092(8)	0.0090(7)	−0.0028(6)	−0.0015(6)	0.0012(6)
	0.011(2)	0.015(3)	0.0130(17)	−0.0046(17)	−0.0053(15)	0.0033(19)

<sup>a</sup> e.s.d.'s in parentheses.**Table 4.** Selected Interatomic Distances (in pm) in  $Ca_7[GeN_4]N_2$  and in  $Sr_7[GeN_4]N_2$ <sup>a</sup>

N1-Centered Distorted Octahedron							
N1-	Ge1	189.9(2)	N1-	Ge1	192.3(5)		
	Ca3	231.3(2)		Sr3	248.6(5)		
	Ca4	247.9(2)		Sr4	261.2(5)		
	Ca2	250.1(2)		Sr2	263.8(5)		
	Ca3	260.5(2)		Sr3	275.6(5)		
	Ca1	263.8(2)		Sr1	278.3(5)		
N2-Centered Distorted Trigonal Prism							
N2-	Ca2	237.6(2)	N2-	Sr2	253.6(5)		
	Ca1	239.4(2)		Sr1	256.6(5)		
	Ca2	243.9(2)		Sr2	262.9(5)		
	Ca1	246.9(2)		Sr1	263.8(5)		
	Ca3	247.9(2)		Sr3	265.0(5)		
	Ca3	248.1(2)		Sr3	265.4(5)		
N3-Centered Distorted Octahedron							
N3-	Ge1	187.8(2)	N3-	Ge1	192.3(5)		
	Ca1	235.1(2)		Sr1	252.5(5)		
	Ca2	251.8(2)		Sr2	264.1(5)		
	Ca4	255.5(2)		Sr4	273.8(5)		
	Ca3	274.3(0)		Sr3	289.8(5)		
Ge1-Centered Tetrahedron							
Ge1	N3	187.8(2)	2×	Ge1	N3	192.2(4)	2×
	N1	189.9(2)	2×		N1	192.3(5)	2×
AE1-Centered Distorted Trigonal Prism							
Ca1	N3	235.1(2)	Sr1	N3	252.6(4)		
	N2	239.4(2)		N2	256.5(5)		
	N2	246.9(2)		N2	263.8(5)		
	N1	263.8(2)		N1	278.3(4)		
	N3	297.5(2)		N3	308.4(5)		
AE2-Centered Distorted Trigonal Prism							
Ca2	N2	237.6(2)	Sr2	N2	253.5(5)		
	N2	243.9(2)		N2	262.9(4)		
	N1	250.1(2)		N1	263.9(4)		
	N3	251.8(2)		N3	264.1(5)		
	N3	285.4(2)		N3	312.8(5)		
AE3-Centered Distorted Trigonal Prism							
Ca3	N1	231.3(2)	Sr3	N1	248.7(4)		
	N2	247.9(2)		N2	265.0(5)		
	N2	248.1(2)		N2	265.5(5)		
	N1	260.5(2)		N1	275.7(5)		
	N3	274.3(2)		N3	289.6(5)		
AE4-Centered Distorted Tetrahedron							
Ca4	N1	247.9(2)	2×	Sr4	N1	261.2(5)	2×
	N3	255.5(2)	2×		N3	273.8(5)	2×

<sup>a</sup> e.s.d.'s in parentheses.

four anions in those compounds are 258–283 pm and thus comparable with the distances Sr–N for Sr4 in  $Sr_7[GeN_4]N_2$ .

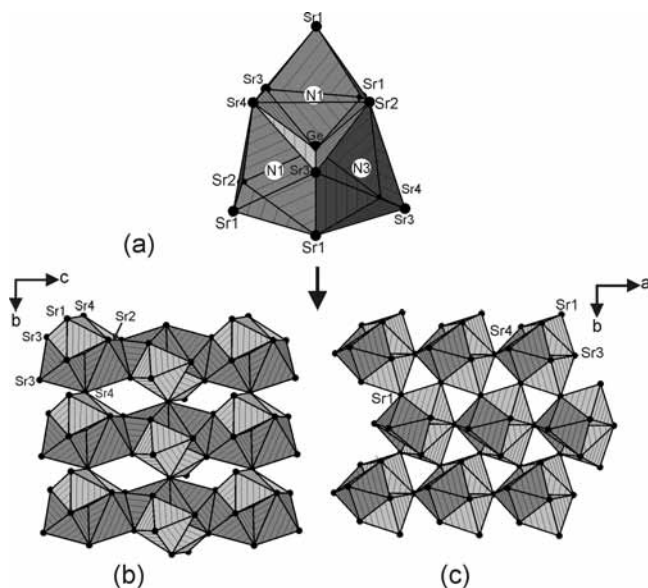


**Figure 1.** (a) Unit cell of  $Sr_7[GeN_4]N_2$  viewed along  $[0\bar{1}0]$ . The alternating  $GeN_{4/2}$  (white polyhedra) and  $SrN_{4/2}$  tetrahedrons (dark polyhedra) forming one-dimensional chains are depicted. The discrete nitrogen atoms (gray spheres) and the  $Sr^{2+}$  ions are also shown (black spheres). (b) Interatomic distances and angles (in pm) of the alternating tetrahedrons, some atoms are shown as ellipsoids at 90% probability level (e.s.d.'s are omitted for clarity, they are  $<0.5$  pm and  $<0.1^\circ$ , respectively). Dashed lines denote the repeating unit of  $\frac{1}{2}[GeSrN_4]$ .

The chains  $\frac{1}{2}[GeSrN_4]$  of alternating edge-sharing  $SrN_4$  and  $GeN_4$  tetrahedrons in  $Sr_7[GeN_4]N_2$  extend along  $[0\bar{1}0]$  (cf. Figure 1b). Quite similar chains are known from  $Sr_3GeMgN_4$ ,<sup>28</sup> where  $Mg^{2+}$  and  $Ge^{4+}$  are in the centers of the tetrahedrons and  $Sr^{2+}$  balances the charge between the chains. The distances Ge–N and Mg–N are comparable (Ge–N: 189 and 192 pm; Mg–N: 203 and 213 pm), in contrast to the distances in the chains of  $Sr_7[GeN_4]N_2$ , where small  $GeN_{4/2}$  tetrahedrons alternate with a significantly elongated  $SrN_{4/2}$  tetrahedrons. The other three crystallo-

(28) Park, D. G.; Gál, Z. A.; DiSalvo, F. J. *J. Alloys Compd.* **2003**, *360*, 85.





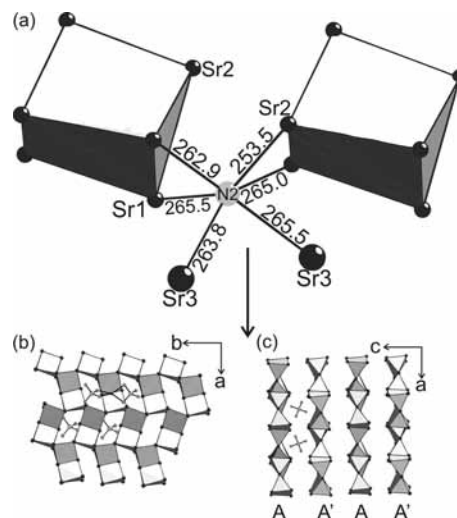
**Figure 2.** Representation of a  $[\text{GeN}_4\text{Sr}_{12}]^{16+}$  unit as condensed  $\text{N}^{3-}$  ion centered distorted octahedral units (c). (b, c) Interconnection of the clusters in different projections.

graphically independent  $\text{Sr}^{2+}$  ions (Sr1, Sr2, Sr3) exhibit coordination number five. The distances Sr–N are between 248.6(4) and 312.8(5) pm, which is within the usual range for nitridic strontium compounds.<sup>4,29</sup>

An alternative description of the crystal structure of  $\text{Sr}_7[\text{GeN}_4]\text{N}_2$  may be achieved by employment of polyhedral units. Many compounds synthesized in metal melts have been rationalized on the basis of anion-centered polyhedrons in contrast to the structure description of oxides, which are usually represented by cation-centered polyhedrons.

In  $\text{Sr}_7[\text{GeN}_4]\text{N}_2$ , both N1 and N3 are six-coordinated by five Sr atoms and one Ge atom arranged as a compressed octahedron with equatorial distances N–Sr ranging from 261.2(5) to 308.5 pm and axial distances from 192.2(4) pm to 252.6(5) pm (cf. Figure 2a), yielding  $[\text{Sr}_{12}\text{GeN}_4]^{16+}$  building blocks. These blocks are connected via edges to form one-dimensional rods extending along [001], which are formally interconnected to yield slabs via the Sr4 atoms that exhibit the low coordination number (cf. Figure 2b). The slabs of  $[\text{Sr}_{12}\text{GeN}_4]^{16+}$  units are further condensed to build up a three-dimensional framework via Sr1 by corner sharing (cf. Figure 2c). An analogous building block  $[\text{Sr}_{12}\text{GeN}_3]^{18+}$  is found in  $\text{Sr}_3\text{GaN}_3$ ,<sup>22</sup> Ga is three-coordinated by N atoms in trigonal planar fashion, and this entity is surrounded by twelve  $\text{Sr}^{2+}$  ions. Again, these polyhedral units can also be viewed as consisting of three anion centered octahedrons. These building blocks are interconnected by edge sharing and corner sharing via one symmetrically independent  $\text{Sr}^{2+}$  ion which exhibits coordination number five.

An octahedral coordination of  $\text{N}^{3-}$  is usually observed for the  $\text{N}^{3-}$  ion while a trigonal prismatic coordination is quite uncommon and has been observed in very few metal nitrides (e.g., WN).<sup>30</sup> Metaprismatic (between octahedral and trigonal



**Figure 3.** Coordination around the N2 atom generates a trigonal prism  $\text{Sr}_6\text{N}$  (a). These trigonal prisms are interconnected by edge-sharing and form layers in [110] (b). The layers are stacked on top of each other and (AA'AA'...) (c). The position of some  $\text{GeN}_4$  tetrahedrons are depicted for easier comparison with Figure 1.

prismatic) coordination of  $\text{N}^{3-}$  as in  $\text{Hf}_3\text{N}_4$  is also very rare.<sup>31</sup> The discrete N2 atom in the structure of  $\text{Sr}_7[\text{GeN}_4]\text{N}_2$  is surrounded by six  $\text{Sr}^{2+}$  ions forming a distorted trigonal prism. Each of these trigonal prisms is connected to three other ones by edge-sharing which results in layers parallel to (110) (cf. Figure 3). The layers are stacked along [001] in an alternating manner (AA'AA'...). Within these layers, the distances Sr–N (253.5(5)–265.5(5) pm) are relatively short.<sup>4,29</sup> In  $\text{Sr}_6\text{GaN}_5$ ,<sup>22</sup> which contains slabs built up by  $[\text{Sr}_6\text{N}]$  octahedrons, the distances Sr–N (259 pm) correspond with the average value of those in  $\text{Sr}_7[\text{GeN}_4]\text{N}_2$ . The N3 polyhedrons in  $\text{Sr}_7[\text{GeN}_4]\text{N}_2$  are connected to N2 prisms by a relatively long (312.8(5) pm) dative contact to Sr2 which also connects the N atoms of the above-mentioned  $[\text{Sr}_{12}\text{GeN}_4]^{16+}$  “clusters” with the discrete N atoms. This effect might stabilize the structure.

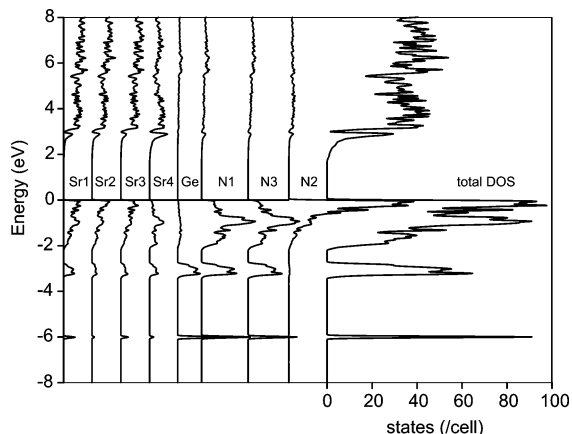
Generally, very little is known about the reaction mechanisms in melts or solutions and the preorganization of building blocks in the liquid phase. The crystal structure  $\text{AE}_7[\text{GeN}_4]\text{N}_2$  (AE = Sr, Ca) consists of both units  $[\text{AE}_6\text{N}]$  and  $[\text{AE}_5\text{XN}]$ , which might support the assumption that N-centered octahedrons of alkaline-earth atoms may have an intrinsic stability. This may be corroborated by the fact that alkaline earth metals increase the solubility of nitrogen in Na melts.<sup>7,8</sup> Alternatively,  $\text{GeN}_4$  tetrahedrons might occur in the metal melt as well.

**DFT Calculations.** LMTO band structure calculations were performed to analyze the electronic structure and chemical bonding of  $\text{Sr}_7[\text{GeN}_4]\text{N}_2$ . The total density-of-states (DOS) and its decomposition into contributions of individual atoms (PDOS) are depicted in Figure 4. The calculated band gap of  $\sim 1.8$  eV is in agreement with the transparency of the compound, but smaller than the  $\sim 2.3$  eV corresponding to the complementary color of the intrinsic red color of the crystals; however, it is well-known that band gaps calculated

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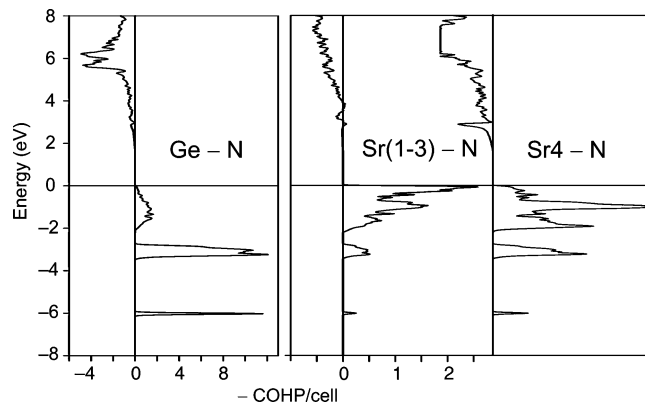


**Figure 4.** Density-of-states of  $Sr_7[GeN_4]N_2$ . The total DOS and the PDOS of all atoms are shown.

with DFT methods are generally too small. The DOS in the proximity of the Fermi level is mainly dominated by the 2p-levels of the N2 atoms, whereas the contributions of the N1- and N3-atoms are at somewhat lower energies. This is attributed to the environment of the N2-atoms, which are not connected to Ge as the N1- and N3-atoms are, but surrounded by Sr atoms only. Furthermore, the N1- and N2-PDOS show strong mixing of the N-2p with the Ge-4p orbitals as seen from the peak at around  $-3$  eV, which is also present in the Ge-PDOS, but not in the N2-PDOS. Thus only the N2 atom can be considered as a true  $N^{3-}$  nitride ion.

The PDOS of the four crystallographically different Sr atoms are very similar, but nevertheless we find a somewhat different PDOS of the Sr4 atom, which may be attributed to the unusual 4-fold coordination. However, we see no reliable reasons to assign a different charge to the Sr4 atom in comparison with Sr(1–3).

The mixing of the Ge-4p orbitals with the N1–2p and N3–2p orbitals argues for a strong covalent character of the Ge–N bonds within the  $GeN_4$  tetrahedrons. This is supported by the COHP diagram in Figure 5 (left), which shows very strong Ge–N bonds. Exclusively bonding states are occupied as expected for the closed-shell nitride compound. A comparison of the Sr(1–3)–N bonds and the Sr(4)–N bonds reveals a noticeable difference (cf. Figure 5, right). This is mainly ascribed to the fact, that Sr(4) is coordinated by the N1- and N3-atoms only. The less nitridic character of these N atoms may be connected with the stability of the otherwise rather unusual 4-fold coordination of strontium in  $Sr_7[GeN_4]N_2$ .



**Figure 5.** COHP diagrams of the Ge–N bonds and different Sr–N bonds in  $Sr_7[GeN_4]N_2$ .

## Conclusion

The structures of the nitridogermanate nitrides  $AE_7[GeN_4]N_2$  ( $AE = Sr, Ca$ ) have two uncommon building blocks: discrete  $N^{3-}$  ions that are coordinated exclusively by  $AE^{2+}$  and additional  $AEN_4$  tetrahedrons that alternate and share edges with isolated  $GeN_4$  tetrahedrons to form chains. While the observed low coordination number four for the small  $Ca^{2+}$  ion is not unusual, only some cases for the larger  $Sr^{2+}$  have been reported in the literature.<sup>10,11</sup> The discrete  $N^{3-}$  ions are 6-fold coordinated in a distorted trigonal prismatic fashion, which is also rarely observed. DFT calculations shows strongly covalent Ge–N bonds and ionic nitride bonds for the discrete  $N^{3-}$  bonds. Despite its low coordination number, Sr4 is energetically similar to the other Sr atoms. With  $AE_7[GeN_4]N_2$  ( $AE = Ca, Sr$ ) we have found nitridogermanate nitrides with a high N/Ge ratio and thus might be valuable as reactive starting materials. Isolated  $GeN_4$  tetrahedrons could further condense under suitable conditions and form a higher condensed nitridogermanate network.

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**Supporting Information Available:** X-ray crystallographic information files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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