

Synthesis and Structure of $\text{Sr}_6\text{Ge}_5\text{N}_2$ and $\text{Ba}_6\text{Ge}_5\text{N}_2$

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Two isostructural new alkaline earth germanium nitrides, $\text{Sr}_6\text{Ge}_5\text{N}_2$ and $\text{Ba}_6\text{Ge}_5\text{N}_2$, were obtained as single crystals from constituent elements in molten Na. They both crystallize in space group P_{mmn} (No. 59) with $a = 4.0007(8)$, $b = 17.954(3)$, $c = 9.089(2)$ Å, $Z = 2$, and $a = 4.1620(2)$, $b = 18.841(1)$, $c = 9.6116(5)$ Å, $Z = 2$, for $\text{Sr}_6\text{Ge}_5\text{N}_2$ and $\text{Ba}_6\text{Ge}_5\text{N}_2$, respectively. Their crystal structure contains features for both Zintl and nitride phases: zigzag anionic chain of ∞Ge^{2-} , and dumbbell-shaped bent anion of GeN_2^{4-} . Counter cations of Sr or Ba wrap these anionic units in a channel-like arrangement. Unlike in other germanium nitrides, bond lengths of both Ge-N arms of the GeN_2^{4-} , are same in $\text{Sr}_6\text{Ge}_5\text{N}_2$ and $\text{Ba}_6\text{Ge}_5\text{N}_2$.

Key Words : Strontium germanium nitride, Barium germanium nitride, Zintl anion

Introduction

By various synthetic routes, a range of many new ternary and quaternary nitrides have been synthesized, and well documented in a number of articles.¹⁻¹⁰ Particularly, by using molten Na as a flux, many new nitrides with interesting structures and properties have been synthesized in recent years.¹¹⁻²⁰ In obtaining these metal nitrides, alkaline earth metal was often added in Na melt to enhance the solubility of nitrogen, and eventually incorporated in the nitride products. In most cases, the nitride products contained nitridometallate anions whose charge was counter balanced by alkaline earth cations.

The metal nitrides exhibit structural features that are quite different from those in metal oxides. Whereas only corners are shared in tetrahedral oxides of Si or Ge, corresponding tetrahedral nitridometallates can share their edges. Tetrahedral units of $[\text{GeN}_4]$ were sharing their edges with tetrahedral neighbors of $[\text{MgN}_4]$ in $\text{Sr}_3\text{GeMgN}_4$.²¹ The first example of edge-sharing $[\text{GeN}_4]$ was demonstrated in $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$.²² Ca_4GeN_4 contains isolated tetrahedral anions of $[\text{GeN}_4]$, and $\text{Ca}_5\text{Ge}_2\text{N}_6$ has infinite chains of corner-shared $[\text{GeN}_4]$.¹³ Known alkaline earth germanium nitrides often contain 'dumbbell-shaped' angular nitridogermanate anions. Most of the known ternary germanium nitrides, such as $\text{Ba}_3\text{Ge}_2\text{N}_2$,²⁰ Ba_2GeGaN ,¹⁵ Ca_2GeN_2 ,¹³ $\text{Sr}_3\text{Ge}_2\text{N}_2$,¹⁷ Sr_2GeN_2 ,¹⁷ or $\beta\text{-Sr}_2\text{GeN}_2$ ²³ contain 'dumbbell-shaped' GeN_2^{4-} anions. Not only the bent anions, $\text{Ba}_3\text{Ge}_2\text{N}_2$,²⁰ also contains zigzag Zintl anions of Ge^{2-} . In this study we report structure of $\text{Sr}_6\text{Ge}_5\text{N}_2$ and $\text{Ba}_6\text{Ge}_5\text{N}_2$, which contains bent anions of GeN_2^{4-} together with zigzag Zintl anions of Ge^{2-} .

Experimentals

$\text{Sr}_6\text{Ge}_5\text{N}_2$ was synthesized from constituent elements which were dissolved in Na melt. Under argon in a VAC

dry-box, NaN_3 (76.1 mg, Aldrich, 99%), Na (81.0 mg, Aldrich, 99%), Ge (17.4 mg, Cerac, 99.999%), Sr (20.4 mg, Aldrich, 99+%), and Li (0.8 mg, Aldrich, 99.9%) were loaded in a Nb container, which was made by welding one end of Nb tubing (110 mm long, 9.5 mm od and 1mm thickness) in an argon atmosphere. The molar ratio of Na : Ge : Sr : Li was 20 : 1 : 1 : 0.5. Other end of the container was subsequently closed by welding in an argon atmosphere, using a Centorr Associates arc furnace. The Nb container was put into silica tubing and sealed under vacuum, to protect the metal container from being oxidized during heat treatment. The reaction container was heated in a muffle furnace at a rate of 50 °C/h to 760 °C. The temperature was then maintained at 760 °C for 48 h, and lowered linearly to 200 °C over 200 h. Thereafter, the furnace was cooled down to room temperature by turning it off. Before the solid products (crystals) were retrieved from the container, Na was separated from them by sublimation at 300 °C under a dynamic vacuum. The crystals were collected into a vial in an argon atmosphere without any further treatment.

$\text{Ba}_6\text{Ge}_5\text{N}_2$ was synthesized via same procedure above, except for the reaction mixture. The reaction mixture for the synthesis of $\text{Ba}_6\text{Ge}_5\text{N}_2$ was prepared by loading NaN_3 (91.2 mg, Aldrich, 99%), Na (201.9 mg, Aldrich, 99%), Ge (79.8 mg, Cerac, 99.999%), Ba (152.6 mg, Aldrich, 99+%), and Li (7.5 mg, Aldrich, 99.98%) in a Nb container, under argon in a VAC dry-box. The molar ratio of Na : Ge : Ba : Li was 10 : 1 : 1 : 1.

The solid product was immersed in poly(butene) oil, and a single crystal in a proper size was chosen under optical microscope. A single crystal of $\text{Sr}_6\text{Ge}_5\text{N}_2$ (or $\text{Ba}_6\text{Ge}_5\text{N}_2$) was mounted in a drop of poly(butene) oil sustained in a plastic loop. The position of the crystal was fixed by solidifying the oil by flowing cold nitrogen gas over the sample. The gas flow also protected the sample from contact with air. X-ray diffraction data were collected with a Bruker SMART system with a CCD detector, and SAINT software was used for integration of the diffraction data.²⁴ An empirical

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absorption correction was applied using SADABS.²⁵ The structure was solved by the direct method, using SHELXS.²⁶ Refinement of the structure was carried out by the full-matrix least square method (on F^2), using SHELXL.²⁶ The atomic parameters were standardized by using STRUCTURE TIDY.²⁷ The space group was verified by using ADDSYM.²⁸ WDX (wavelength dispersive X-ray) and semi-quantitative (without a standard) EDX (energy dispersive X-ray) analysis were carried out by using a JEOL JXA-8900R WD/ED combined microanalyzer.

Results and Discussion

The product from Sr-containing reaction mixture was obtained as glistening black powder. When observed under a microscope it was black needles mixed with some red chunks of unknown solid. When exposed in air, those crystals and solids readily decomposed and produced NH_3 , indicating they are nitrides. In poly(butene) oil, they could be handled for a few days without any significant degradation. Indexing the single crystal diffraction peaks indicated the black tetragonal prismatic needle is a new ternary nitride. The new crystal has unit cell volume of $652.8(2) \text{ \AA}^3$. It belongs to the orthorhombic, and has unit cell parameters of $a = 4.0007(8)$, $b = 17.954(3)$, and $c = 9.089(2) \text{ \AA}$. The tetragonal prism of $\text{Sr}_6\text{Ge}_5\text{N}_2$ was elongated along b-axis into a needle. The Sr to Ge ratio obtained by semi-

quantitative EDX (energy dispersive X-ray) analysis on several black needles fell in the range of 5.3 : 5 to 5.6 : 5, which suggests the ratio 6 : 5 of a new ternary nitride, $\text{Sr}_6\text{Ge}_5\text{N}_2$. Discrepancy in the values is presumed to be caused by decomposition of the samples occurred readily in the e-beam. N was qualitatively identified by WDX (wavelength dispersive X-ray) analysis.

Systematic extinctions suggested the space group P_{mnm} (No. 59). A starting structural model was obtained for heavy atoms (Sr and Ge) by the direct method in P_{mnm} . N was located in the early stages of the refinement of the starting model. The final refinement was obtained with $R_1 = 3.9\%$.

The product from Ba-containing reaction mixture was obtained as thin rectangular prism in metallic black. The crystal was thin along c direction, whose ab-surface had linear texture running along b-axis. Though the crystal could be handled in poly(butene) oil without significant degradation, it readily decomposed in air and produced NH_3 . Indexing the single crystal diffraction peaks indicated that the black crystal is also a new ternary nitride. The new crystal has unit cell volume of $753.7(1) \text{ \AA}^3$. It belongs to the orthorhombic, and has unit cell parameters of $a = 4.1620(2)$, $b = 18.841(1)$, and $c = 9.6116(5) \text{ \AA}$. The Ba to Ge ratio obtained by semi-quantitative EDX and WDX analysis on the crystal gave very similar values obtained for $\text{Sr}_6\text{Ge}_5\text{N}_2$.

Systematic extinctions suggested the space group P_{mnm} (No. 59). A starting structural model was obtained for heavy

Table 1. Crystallographic data for $\text{Sr}_6\text{Ge}_5\text{N}_2$, and $\text{Ba}_6\text{Ge}_5\text{N}_2$

	$\text{Sr}_6\text{Ge}_5\text{N}_2$	$\text{Ba}_6\text{Ge}_5\text{N}_2$
Crystal system	Orthorhombic	Orthorhombic
Space group	P_{mnm} (No. 59)	P_{mnm} (No. 59)
a / Å	4.0007(8)	4.1620(2)
b / Å	17.954(3)	18.841(1)
c / Å	9.089(2)	9.6116(5)
V / Å^3	652.8(2)	753.70(7)
Z	2	2
D (calcd) / g cm^{-3}	4.663	5.354
T / K	173(2)	173(2)
Formula weight	916.69	1215.01
Wavelength / Å	0.71073	0.71073
Abs. Coeff. / mm^{-1}	35.579	25.166
F(000)	804	1020
Crystal size / mm^3	$0.02 \times 0.10 \times 0.02$	$0.05 \times 0.05 \times 0.02$
θ / degree	2.24 to 29.55	2.16 to 36.32
Index ranges	$-5 \leq h \leq 5, -24 \leq k \leq 24, -9 \leq l \leq 12$	$-5 \leq h \leq 6, -29 \leq k \leq 30, -5 \leq l \leq 16$
Refln. collected	5695	8826
Independent refln.	1057 [R(int) = 0.0587]	1965 [R(int) = 0.0376]
Data / restraints / parameters	1057/0/44	1965/0/44
Goodness-of-fit on F^2	1.140	1.323
Final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.0322, wR_2 = 0.0721$	$R_1 = 0.0524, wR_2 = 0.0959$
R indices (all data)	$R_1 = 0.0390, wR_2 = 0.0749$	$R_1 = 0.0606, wR_2 = 0.0978$
Extinction coefficient	0.0032(4)	0.00102(13)
Largest diff. peak and hole / e.Å^{-3}	1.451 and -1.351	4.454 and -3.296

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, where $w = 1 / \sigma(F_o^2) + (gP)^2 + jP$, $P = [\max(F_o^2, 0) + 2F_c^2] / 3$, $g = 0.0371$, $j = 1.5865$ for $\text{Sr}_6\text{Ge}_5\text{N}_2$, and $g = 0.0266$, $j = 16.0981$ for $\text{Ba}_6\text{Ge}_5\text{N}_2$.

Table 2. Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters for Sr₆Ge₅N₂

atom	sites	x	y	z	U _{eq} ^a
Sr(1)	4e	2500	660(1)	1143(1)	7(1)
Sr(2)	4e	2500	6098(1)	5360(1)	8(1)
Sr(3)	2b	2500	7500	8414(1)	8(1)
Sr(4)	2a	2500	2500	7572(1)	12(1)
Ge(1)	4e	2500	555(1)	7380(1)	8(1)
Ge(2)	4e	2500	6195(1)	1437(1)	9(1)
Ge(3)	2a	2500	2500	4193(1)	8(1)
N	4e	2500	1667(3)	2943(7)	9(1)

^aThe equivalent isotropic thermal displacement parameter, U_{eq} in Å³ × 10⁻³ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters for Ba₆Ge₅N₂

atom	sites	x	y	z	U _{eq} ^a
Ba(1)	4e	2500	668(1)	1113(1)	9(1)
Ba(2)	4e	2500	6096(1)	5357(1)	8(1)
Ba(3)	2b	2500	7500	8474(1)	9(1)
Ba(4)	2a	2500	2500	7561(1)	10(1)
Ge(1)	4e	2500	569(1)	7395(1)	10(1)
Ge(2)	4e	2500	6175(1)	1534(1)	10(1)
Ge(3)	2a	2500	2500	4104(1)	8(1)
N	4e	2500	1694(4)	2928(8)	9(1)

^aThe equivalent isotropic thermal displacement parameter, U_{eq} in Å³ × 10⁻³ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Anisotropic displacement parameters (Å³ × 10⁻³) for Sr₆Ge₅N₂. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Sr(1)	6(1)	6(1)	10(1)	-1(1)	0	0
Sr(2)	7(1)	7(1)	10(1)	-1(1)	0	0
Sr(3)	7(1)	7(1)	11(1)	0	0	0
Sr(4)	15(1)	7(1)	15(1)	0	0	0
Ge(1)	6(1)	8(1)	11(1)	0(1)	0	0
Ge(2)	6(1)	7(1)	15(1)	1(1)	0	0
Ge(3)	10(1)	5(1)	10(1)	0	0	0
N	8(2)	4(2)	15(3)	-4(2)	0	0

atoms (Ba and Ge) by the direct method in P_{mmn}. N was located in the early stages of the refinement of the starting model. The new ternary barium nitride, Ba₆Ge₅N₂, was isostructural with Sr₆Ge₅N₂. The final refinement was obtained with R₁ = 6.1%. Crystallographic data on Sr₆Ge₅N₂ and Ba₆Ge₅N₂ are summarized in Table 1 through 6.

Figure 1a shows crystal structure of Sr₆Ge₅N₂. Comparison of the crystallographic data indicates the crystal structures of Sr₆Ge₅N₂ and Ba₆Ge₅N₂ are almost identical except the dimensional values are larger for Ba₆Ge₅N₂ than those for Sr₆Ge₅N₂ in consistent extent. Therefore, figures and structural descriptions for Sr₆Ge₅N₂ shall be applied also to Ba₆Ge₅N₂ in same manner, and they will not be dealt

Table 5. Anisotropic displacement parameters (Å³ × 10⁻³) for Ba₆Ge₅N₂. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Ba(1)	9(1)	10(1)	8(1)	-2(1)	0	0
Ba(2)	7(1)	9(1)	9(1)	-1(1)	0	0
Ba(3)	8(1)	11(1)	7(1)	0	0	0
Ba(4)	10(1)	9(1)	11(1)	0	0	0
Ge(1)	8(1)	12(1)	10(1)	0(1)	0	0
Ge(2)	7(1)	10(1)	13(1)	-1(1)	0	0
Ge(3)	11(1)	7(1)	6(1)	0	0	0
N	9(4)	7(3)	12(3)	-4(3)	0	0

Table 6. Selected atomic separation [Å] and bond angles [degree] in Sr₆Ge₅N₂, and in Ba₆Ge₅N₂

(Sr ₆ Ge ₅ N ₂)			
Sr1-N	2.4390(9)	Sr2-N	2.725(4)
Sr3-N	2.785(4)		
Sr4-Ge1	3.496(1)	Sr4-Ge2	3.2105(8)
Sr4-Ge3	3.071(2)		
Ge3-N	1.878(6)	N-Ge3-N	105.5(4)
Ge1-Ge2	2.5445(7)	Ge-Ge-Ge	103.66(4)
(Ba ₆ Ge ₅ N ₂)			
Ba1-N	2.604(8)	Ba2-N	2.884(6)
Ba3-N	2.908(6)		
Ba4-Ge1	3.642(1)	S4-Ge2	3.3643(9)
Ba4-Ge3	3.323(2)		
Ge3-N	1.893(8)	N-Ge3-N	106.7(5)
Ge1-Ge2	2.5873(9)	Ge-Ge-Ge	107.09(5)

separately. The structure has two major structural units containing Ge. 'Dumbbell-shaped' bent anions of GeN₂⁴⁻ are stacked along a-axis, and zigzag chains of Zintl anionic Ge²⁻ are running along the same axis. Anionic charge of those two structural units is counter balanced by surrounding Sr cations. The zigzag chains of Ge²⁻ are found in the Zintl compound of BaGe₅,²⁹ and also observed in ternary nitride compounds of Sr₃Ge₂N₂¹⁷ and Ba₃Ge₂N₂.²⁰ From the structure of Sr₆Ge₅N₂, oxidation state of Ge can be formulated as [Sr₆Ge(1)²⁻Ge(2)²⁻]⁴⁺[Ge(3)²⁺N₂]⁴⁻, which indicates the compound contains both Zintl and nitride components.

The Ge(1)-Ge(2) bond length and Ge-Ge-Ge bond angle in Sr₆Ge₅N₂ are 2.55 Å and 103.7°, respectively. The Ge(1)-Ge(2) bond length and Ge-Ge-Ge bond angle in Ba₆Ge₅N₂ are 2.59 Å and 107.1°, respectively. They are both smaller than those (2.64 Å and 109.2°) in Ba₃Ge₂N₂.²⁰ The Ge-Ge bond length (2.55 and 2.59 Å) is larger than that of Sr₃Ge₂N₂ (2.45 Å).¹⁷ The anionic zigzag chain is surrounded by Sr cations. Each Ge of the chain is sitting in the middle of the mono-capped trigonal prismatic arrangement of Sr atoms, as shown in Figure 2a. By sharing rectangular faces in alternating manner, the mono-capped trigonal prisms of Sr are condensed into a channel, which the zigzag chain passes

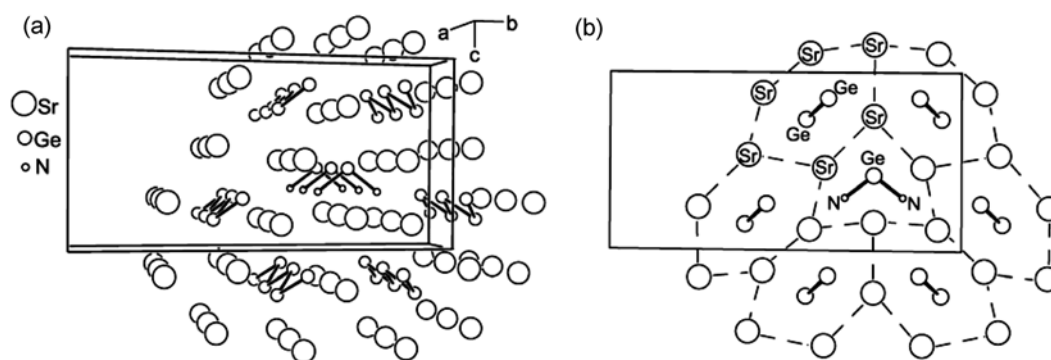


Figure 1. (a) Crystal structure of $\text{Sr}_6\text{Ge}_5\text{N}_2$. The structure of isostructural $\text{Ba}_6\text{Ge}_5\text{N}_2$ is nearly identical with the one for $\text{Sr}_6\text{Ge}_5\text{N}_2$, thereby not shown separately. (b) The structure seen along a-axis shows the channel-like arrangement of Sr (each channel depicted by broken lines) around the anionic structural units containing Ge. The rectangular box is the unit cell outline. Only Ge-Ge and Ge-N bonds were shown to depict the structural components of zigzag Zintl anions of ∞Ge^{2-} , and bent anions of GeN_2^{4-} .

through. When viewed along a-axis in Figure 2b, the zigzag chain is running along the channel generated by those Sr cations. The similar arrangement of alkaline earth cations is also observed in the structure of Zintl compound BaGe ,²⁹ and of $\text{Ba}_3\text{Ge}_2\text{N}_2$,²⁰ whose capped prisms of Ba are condensed into a channel which contains a zigzag chain of Ge^{2-} . Whereas, each channel in $\text{Ba}_3\text{Ge}_2\text{N}_2$ is isolated from others,²⁰ and surrounded by arrays of stacked bent anions of GeN_2^{4-} , those channels in $\text{Sr}_6\text{Ge}_5\text{N}_2$ are connected from side to side, as shown in Figure 1b, by sharing triangular faces of the Sr prisms. View along a-axis in figure 1b shows that an array of stacked GeN_2^{4-} along a-axis is encompassed by six of these inter-connected Sr channels. This observation suggests that $\text{Sr}_6\text{Ge}_5\text{N}_2$ retains most of the structural feature of typical Zintl compounds, whereas it is largely dismantled in $\text{Ba}_3\text{Ge}_2\text{N}_2$.²⁰ It is interesting to note that structural variation is closely related to nitrogen to metal ratio. When nitrogen is added, nitride component is introduced as bent anions of GeN_2^{4-} . Rather than being evenly distributed into the structure, they stacked into an array, breaking apart the channel structure Zintl anions generated (as in $\text{Sr}_6\text{Ge}_5\text{N}_2$). As more nitrogen is added, number of such GeN_2^{4-} arrays increase, and the channel structure is further dismantled (as in $\text{Ba}_3\text{Ge}_2\text{N}_2$),²⁰ until Zintl anion is excluded and GeN_2^{4-} dominates the structure (as in Sr_2GeN_2).^{17,23} As far as nitrogen to germanium ratio remains low, tetrahedral $[\text{GeN}_4]$ doesn't form.

In $\text{Sr}_6\text{Ge}_5\text{N}_2$, the Ge(3)-N bond length is 1.878 Å, and identical for both arms of GeN_2^{4-} , and N-Ge(3)-N bond angle is 105.5°. For $\text{Ba}_6\text{Ge}_5\text{N}_2$, the Ge(3)-N bond length is 1.893 Å, and identical for both arms, and N-Ge(3)-N bond angle is 106.7°. It is interesting to note that Ge-N bonds are identical, which is the first example of ternary germanium nitride which contains a symmetric bent anion of GeN_2^{4-} . In all other germanium nitrides which contain 'dumbbell-shaped' bent anions of GeN_2^{4-} , the bond lengths of both arms are different.^{13,17,20,23} As seen in the Figure 1b, GeN_2^{4-} is sitting in the middle of a symmetric setting (a mirror plane bisecting N-Ge-N) generated by six channel systems inter-connected in very symmetric manner. In known ternary

germanium nitrides, such as $\text{Ba}_3\text{Ge}_2\text{N}_2$,²⁰ $\text{Sr}_3\text{Ge}_2\text{N}_2$,¹⁷ Sr_2GeN_2 ,¹⁷ $\beta\text{-Sr}_2\text{GeN}_2$,²³ Ca_2GeN_2 ,¹³ the 'dumbbell-shaped' GeN_2^{4-} are all placed in surroundings that are not symmetric.

N is coordinated to five Sr and one Ge, generating pseudo-octahedron of $[\text{Sr}_5\text{GeN}]$. Bond length of Sr-N ranges from 2.44 to 2.79 Å. Sr(1)-N bond, which is 2.44 Å, is rather shorter than usual. Sr-N bond length of known germanium nitrides ranges from 2.56 to 2.81 Å,¹⁷ and longer extreme goes up to 2.945 Å.²¹ Two of these octahedra share a face to form a hypothetical structural unit of $[\text{Sr}_8\text{GeN}_2]$, which is shown at lower half in Figure 3a. The unit contains the bent anion of GeN_2^{4-} in it. By sharing side edges, this hypothetical structural unit repeats and generates a strap running along a-axis, as shown in Figure 3b. In previous reports on the structures of various new ternary and quaternary nitrides,^{21-23,30-31} it has been demonstrated that N-centered polyhedral perspective can be useful in systematically visualizing space filling patterns of the crystal structures. But, unlike in other metal nitrides, N-centered polyhedral perspective could not provide space-filling information for $\text{Sr}_6\text{Ge}_5\text{N}_2$, because structural components of Zintl and nitride phases are coexistent. Only nitride part of the structure could be represented by N-polyhedra. By comparing the structure of $\text{Sr}_6\text{Ge}_5\text{N}_2$ (or $\text{Ba}_6\text{Ge}_5\text{N}_2$) with that of $\text{Ba}_3\text{Ge}_2\text{N}_2$,²⁰ variation of structural features accompanied by a change in composition can be deduced. In $\text{Ba}_3\text{Ge}_2\text{N}_2$, the hypothetical structural unit of $[\text{Ba}_8\text{GeN}_2]$ repeats itself to generate two dimensional layers,²⁰ rather than those isolated straps seen in the Figure 3b for $\text{Sr}_6\text{Ge}_5\text{N}_2$ and $\text{Ba}_6\text{Ge}_5\text{N}_2$. As nitrogen to metal ratio increases (0 : 2 for BaGe , 2 : 11 for $\text{Sr}_6\text{Ge}_5\text{N}_2$, 2 : 5 for $\text{Ba}_3\text{Ge}_2\text{N}_2$, and 2 : 3 for Sr_2GeN_2), more GeN_2^{4-} are introduced into the structure. Consequently, less feature of the Zintl compound is left. As nitride component increases, the structure generated by N-polyhedra increases from one dimensional straps in $\text{Sr}_6\text{Ge}_5\text{N}_2$ to two dimensional layers in $\text{Ba}_3\text{Ge}_2\text{N}_2$.²⁰ As can be expected, N-polyhedra generate three dimensional network structures with no Zintl phase in Sr_2GeN_2 .

Coordination around Sr(4) in Figure 3a is interesting to note. In known ternary nitrides, alkaline earth is coordinated

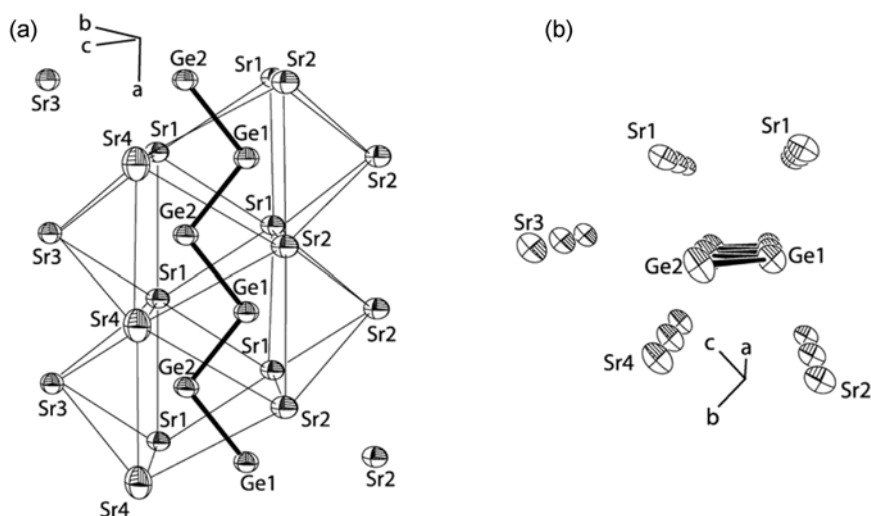


Figure 2. (a) The channel-like arrangement of Sr around zigzag anion of ∞Ge^{2-} . Mono-capped prisms of Sr collapse into such arrangement by sharing rectangular side faces in alternating manner. (b) The view along a-axis shows that the zigzag anion passes through the Sr channel.

by as many as four to seven nitrogens.^{11-19,21-23,30-31} As an example of unusual coordination, Ba was reported to be coordinated only by two nitrogens in $\text{Ba}_3\text{Ge}_2\text{N}_2$.²⁰ In $\text{Sr}_6\text{Ge}_5\text{N}_2$, no nitrogen is coordinated to Sr(4). Nearest neighbors around Sr(4) are all Ge. Seven Ge are coordinated to Sr(4) in a distance of 3.210, 3.496, and 3.071 Å for Ge(2), Ge(1), and Ge(3), respectively. Direct evidence of the electron density in the vacant region around Sr(4) cannot be obtained by diffraction technique used in this study. But considering octet rule and electron counting, it is suggested that non-bonding electron pairs of Ge complete the coordination sphere. The Sr(4) drew much nearer to Ge(3) (in a distance of 3.071 Å), suggesting coordination of the Sr to the lone pair on Ge, as seen in the precedent example of $\text{Ba}_3\text{Ge}_2\text{N}_2$.²⁰

In summary, the new ternary germanium nitrides, $\text{Sr}_6\text{Ge}_5\text{N}_2$ and $\text{Ba}_6\text{Ge}_5\text{N}_2$, are isostructural, and contain both zigzag Zintl anion of Ge^{2-} and ‘dumbbell-shaped’ bent anion of GeN_2^{4-} . These anionic structural units are surrounded by

Sr (or Ba) in a channel-like arrangement, generated by structural unit of mono-capped prisms of Sr (or Ba). Placed in a symmetric site surrounded by the Sr channels, Ge-N bond length in the bent anion is identical, which is the first example of a symmetric GeN_2^{4-} . As a rare example in ternary nitrides, these new nitrides contain Sr (or Ba) which is coordinated to no nitrogen at all. Instead, seven Ge are coordinated to Sr (or Ba). By addition of $\text{Sr}_6\text{Ge}_5\text{N}_2$ and $\text{Ba}_6\text{Ge}_5\text{N}_2$ on the list of known germanium nitrides, comparison of the structure could be made in a rough partial spectrum of compositional range. As far as nitrogen to germanium ratio, and alkaline earth to germanium ratio are both below 2, nitride component appears to be introduced as bent anions of GeN_2^{4-} into Zintl structure. Addition of nitrogen can also be interpreted as the introduction of N-centered pseudo octahedron of $[\text{GeA}_5\text{N}]$, (where A is Sr or Ba). As nitrogen to metal ratio increases (more nitrogen introduced), the structural component of nitride, generated by the pseudo octahedra, stepwise transformed from one

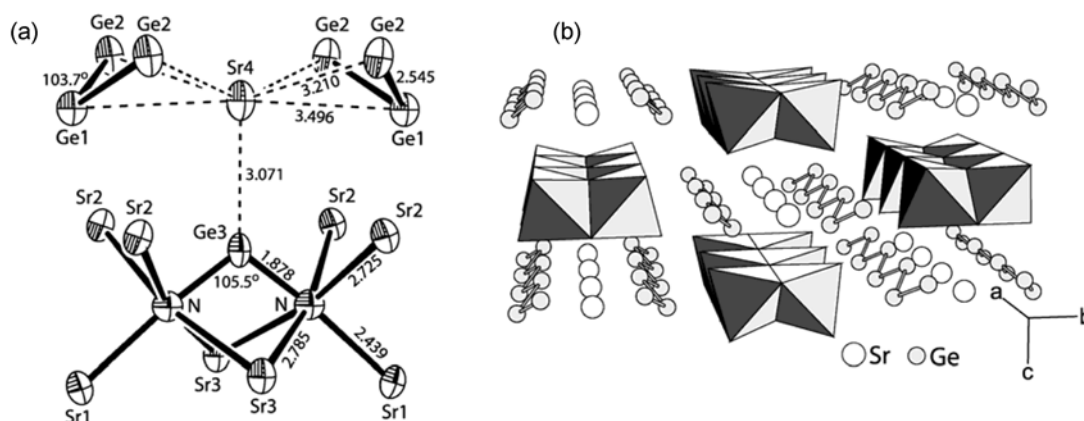


Figure 3. (a) Local coordination around vacant region around Sr(4). Hypothetical structural unit of $[\text{Sr}_8\text{GeN}_2]$, which is generated by face-sharing of two pseudo octahedral $[\text{Sr}_3\text{GeN}]$ is shown in lower half. Coordination around Sr(4) is shown in upper half. (b) Crystal structure of $\text{Sr}_6\text{Ge}_5\text{N}_2$, described by N-centered polyhedral perspective, where those hypothetical structural units of $[\text{Sr}_8\text{GeN}_2]$ are depicted as polyhedra.

dimensional strap, to two dimensional layer, and finally to three dimensional network.

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