$Ba_9Ge_3N_{10}$: A New Ternary Nitride Containing Isolated Planar Triangular Anions of $[GeN_3]^{5-}$

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A new nitride, $Ba_9Ge_3N_{10}$, was obtained as single crystals from constituent elements in molten Na. It crystallizes in space group R-3c (No. 167) with a = 7.9399(2) Å, c = 17.282(1) Å, and Z = 2. It contains the first example of isolated nitridometallate anions of GeN_3^{5-} in perfect planar triangular shape. Ge-N bond length is 1.786(8) Å, which is significantly shorter than any known Ge-N bonds, ranging from 1.84 Å to 1.95 Å. Valence bond model suggests partial multiple bonding character of the Ge-N bond, which is the first example of such bonding configuration for Ge-N bond. N-centered polyhedral perspective suggests the structure of $Ba_9Ge_3N_{10}$ can be conceived as the cationic framework of $[Ba_9Ge_3N_9]^{3+}$, whose 1/3 of the octahedral interstitial sites are occupied by N^{3-} anions.

Key Words : Barium germanium nitrides, Metal nitrides, Nitridometallates

Introduction

Synthesis and characterization of a new nitride compound is challenging and demanding, in part due to their propensity for hydrolysis or oxidation in air. In spite of the obstacles, the field of nitride chemistry has seen rapid growth, recently.[1-10] Numerous new nitride compounds have been obtained via a few different synthetic routes, such as the solid-solid reaction between two different binaries, gas-solid reaction between solid precursors and NH_3, or reaction among reactants dissolved in molten metal. Molten Na has been especially useful in obtaining single crystalline products of a variety of new nitride compounds.[11-20] An alkaline metal is often added to enhance the solubility of nitrogen into Na melt. In most cases, alkaline earth metal is introduced into the new nitride compounds when they were synthesized in molten Na.

Recently, many new ternary and quaternary nitrides, which contain Ge or Ga have been synthesized in Na melt.[21-27] Especially, the number of Ge-containing nitride compounds has grown rapidly so that characteristic features in the structures of the Ge-containing nitrides start to emerge. The structures of those nitrides have been described as isolated or condensed nitridometallate anions surrounded by alkaline earth metal cations. Ge behaves as a typical metalloid, exhibiting a range of formal oxidation states extended from 4– to 4+. Therefore, the structural theme for the Ge-containing nitride compounds is diverse. The formal charges of Ge in nitride compounds known to date are 4+, 2+, 2– and 4–. When Ge has no coordination to nitrogen, it behaves as an isolated anion of Ge^{4-}, which is surrounded by metal cations, as in Ba_2GeGaN,[15] or $Sr_{11}Ge_4N_6$.[25] When Ge is in formal charge of 2-, it extends to Zintl anion of $_\infty^1[Ge]^{2-}$, as in $Sr_3Ge_2N_2$, $Ba_3Ge_2N_2$, $Sr_6Ge_5N_2$, or $Ba_6Ge_5N_2$.[17-24] When Ge is in formal charge of 2+, it coordinates to 2 nitrogens into a dumbbell-shaped anion of $[GeN_2]^{4-}$. Dumbbell-shaped $[GeN_2]^{4-}$ has been observed exclusively as an isolated nitridometallate anion in many nitrides, such as Ca_2GeN_2, Sr_2GeN_2, $Sr_3Ge_2N_2$, $Ba_3Ge_2N_2$, or β-Sr_2GeN_2.[13,17,20,23] When Ge is in formal charge of 4+, it coordinates to 4 nitrogens, generating coordination sphere of tetrahedral $[GeN_4]^{8-}$. Tetrahedral $[GeN_4]^{8-}$ can exist as an isolated nitridometallate anion as in Ca_4GeN_4.[13] It can also extends to edge-shared dimeric anion of $[Ge_2N_6]^{10-}$ in $Li_4Sr_3Ge_2N_6$,[21] or to corner-linked 1D-chain of $_\infty^1[GeN_3]^{5-}$ in $Ca_5Ge_2N_6$.[13] More condensed structures of 2D-sheets or 3D-networks have not been observed, yet. In this study, we report a new Ge-containing ternary nitride compound, $Ba_9Ge_3N_{10}$, which contains the first example of the isolated planar triangular anions of $[GeN_3]^{5-}$ with unusually short Ge-N bonds of 1.786(8) Å.

Experimental

The synthesis of $Ba_9Ge_3N_{10}$ was carried out in a Nb container. The Nb container was made by welding one end of Nb tubing (110 mm long, 9.5 mm od, and 1 mm thick) into a closed bottom. The welding was carried out in an argon atmosphere, using a Centorr Associates arc furnace. Under argon in a VAC dry-box, NaN_3 (65.0 mg, Aldrich, 99%), Na (93 mg, Aldrich, 99%), Ba (206.1 mg, Aldrich, +99%), Ge (36.3 mg, Cerac, 99.999%), Mg (12.2 mg, Aldrich, 99.98%) were loaded in the container. The molar ratio of Na:Ba:Ge:Mg was 10:3:1:1. The container was then sealed by welding the remaining end under argon. In order to protect the Nb-container from oxidation, it was put into silica tubing and sealed under vacuum. The reaction container was then heated in a muffle furnace at a rate of 50 °C/h to 760 °C. The temperature was maintained at the temperature for 48 h, and lowered linearly to 200 °C over 200 h. Once the temperature reached to 200 °C, the furnace was turned off, so that it cooled down to room temperature. The

Na was separated from reaction products by evaporating it at 300 ºC under dynamic vacuum.

A single crystal of $Ba_9Ge_3N_{10}$ in an appropriate size was picked up under microscope from the powdery product immersed in poly(butene) oil. The crystal was mounted in a drop of the oil sustained in a plastic loop. A flow of cold nitrogen gas over the sample solidified the oil, and protected the crystal from contact with air. X-ray diffraction data were collected with a Bruker X8 APEX II diffractometer equipped with 4 K CCD detector. Initial orientation matrix was obtained by using APEX2 program.[28] The integration of the diffraction data was carried out by the program SAINT.[29] An empirical absorption correction was applied using SADABS.[30] The initial input file for solving the crystal structure was prepared by XPREP.[31] The structure was solved by the direct method, using SHELXS.[32] Refinement of the structure was carried out by the full-matrix least square method (on F^2), using SHELXL.[32] The atomic parameters were standardized by using STRUCTURE TIDY.[33] The space group was verified by using ADDSYM.[34] Bond valence and Madelung potential was calculated by EUTAX.[35] WDX (wavelength dispersive X-ray) and semi-quantitative (without standard) EDX (energy dispersive X-ray) analyses were carried out by using a JEOL JXA-8900R WD/ED combined microanalyzer.

Results and Discussion

Product was obtained as silvery powder. The apparent silvery color by bare eyes was misleading, caused by small remnant of Na, which put very thin silvery coating on a portion of crystals. When observed under microscope, crystals in several different shapes and colors were observed. Majority of the crystals were transparent in a range of color from light yellow to brown.[36] Mixed with those transparent crystals, non-transparent black crystals with mostly in a shape of rounded block could be observed. The size of the black crystal was rather small, making it hard to find a crystal in an appropriate dimension for X-ray measurement. Most crystals were obtained as merged together. Only a few crystals reached a size of 50 μm, and had small satellites attached to it. The satellites were physically removed under the microscope as thoroughly as possible before the X-ray diffraction measurement.

Indexing on the single crystal diffraction peaks obtained from the black crystal indicated the crystal is a new compound, which belongs to rhombohedral system, with unit-cell parameters of a = 7.9399, c = 17.2821 Å. Nitrogen was verified from the crystal by observing nitrogen peak by WDS analysis. EDS semi-quantitative analyses were carried out on several black crystals in order to obtain the elemental ratio. Only peaks for Ge and Ba were observed with no other ones related to Mg or Na. The atomic ratio of Ba/Ge was measured to be 2.9 (± 0.05).

Systematic extinctions in the diffraction data suggested the space group of R3c or R-3c. Initial structure solution was obtained by the direct method in space group of R-3c (centro-symmetric). Two crystallographic sites with substantial electron densities were immediately allocated for Ba and Ge. The atomic ratio between Ba and Ge was 3:1, which conforms to the value obtained by EDS analyses. By including N into the solution, structural refinement reached the level of R1 = 3.3%. There still was a residual electron density remained at (0,0,0), even though it was much less for N full occupancy. When partial occupancy of 1/3 by N was applied, the refinement reached R1 = 2.8%. The empirical formula came out to be $Ba_9Ge_3N_{10}$. The sites might have been fully occupied by inadvertently introduced hydride anions. But, structural refinement done with fully occupied hydrides (instead of 1/3-occupied N) gave R1 = 3.2%, which is higher than 2.8%. Moreover, remnant electron density with highest peak of 7.53 at (0,0,0) indicates the element has to be heavier than hydride, which points to N. Crystallographic data on $Ba_9Ge_3N_{10}$ are provided in Table 1-4.

Unit-cell structure of $Ba_9Ge_3N_{10}$ is shown in Figure 1. Ge coordinates to three nitrogens, generating a structural subunit of a triangle, which is shown in Figure 2. Three Ge-N bond lengths are identical to be 1.786(8) Å. Three N-Ge-N angles are all 120 degrees. Therefore, the anion of $[GeN_3]^{5-}$ is in a perfect planar triangular conformation. The triangular anion of $[GeN_3]^{5-}$ is isolated, being separated from other anions by surrounding Ba^{2+} cations. The minimum distance between center to center (Ge to Ge) of neighboring triangles is 5.41 Å. The nearest corner-to-corner (N to N) distance between neighboring triangles is 3.70 Å.

This structural feature has a few unique aspects that are worth to note. The anion of $[GeN_3]^{5-}$ in $Ba_9Ge_3N_{10}$ is the first example of a planar triangular structural subunit con-

Table 1. Crystallographic data for $Ba_9Ge_3N_{10}$

Crystal system	rhombohedral
Space group	R-3c
Unit cell dimensions (Å)	a = 7.9399(2)
	c = 17.2821(11)
Volume (Å^3)	943.53(7)
Z	2
Density (calcd./ mg·m^{-3})	5.610
Temperature (K)	173(2)
Absorption coefficient (mm^{-1})	23.144
F(000)	1340
Crystal size (mm^3)	0.06 × 0.06 × 0.04
Theta range for data collection (°)	3.79 to 36.29
Index ranges	$-12 \le h \le 13$, $-13 \le k \le 13$,
	$-28 \le l \le 27$
Reflections collected	5639
Independent reflections	516 [R(int) = 0.0327]
Data/restraints/parameters	516/0/16
Goodness-of-fit on F^2	1.274
Final R indices [I>2sigma(I)] [a]	R1 = 0.0280, wR2 = 0.0573
R indices (all data) [a]	R1 = 0.0309, wR2 = 0.0580
Extinction coefficient	0.00069(5)
Largest diff. peak and hole (e·Å^{-3})	1.998 and −1.653

[a] $R1 = \Sigma \| Fo | - | Fc \| / \Sigma | Fo |$. $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma (wF_o^2)^2]^{1/2}$, where $w = 1/\sigma(F_o^2)^2 + (gP)^2 + jP]$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$. g = 0.0036, j = 45.4018.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ba_9Ge_3N_{10}$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	Wyckoff	x	y	z	occp	U(eq)
Ba(1)	**18e**	5868(1)	0	2500	1.00	14(1)
Ge(1)	**6a**	0	0	2500	1.00	10(1)
N(1)	**18e**	2249(10)	0	2500	1.00	28(2)
N(2)	**6b**	0	0	0	0.33	4(4)

Table 3. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Ba_9Ge_3N_{10}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba(1)	12(1)	17(1)	16(1)	−3(1)	−2(1)	9(1)
Ge(1)	9(1)	9(1)	12(1)	0	0	5(1)
N(1)	23(3)	26(4)	36(4)	−2(3)	−1(2)	13(2)
N(2)	6(6)	6(6)	1(8)	0	0	3(3)

Table 4. Selected interatomic spacings [Å] and bond angles [degree] in $Ba_9Ge_3N_{10}$

Ge-N(1)	1.786(8)	N(1)-Ge-N(1)	120.00°(0)
Ba-N(1)	2.8451(6)	Ba-N(1)-Ge	87.1°(2)
	2.873(8)		100.5°(2)
	2.982(2)		180.00°(0)
		Ba-N(1)-Ba	79.5°(2)
			79.94°(2)
			92.9°(2)
			101.14°(3)
			159.0°(3)
Ba-N(2)	2.7933(1)	Ba-N(2)-Ba	84.190°(3)
			95.810°(3)
			180.00°(2)

taining Ge in nitrides. In previously known Ge-containing nitride compounds, Ge coordinates to either 4 or 2 nitrogens to generate unique structural subunits of tetrahedral $[GeN_4]^{8-}$ or dumbbell-shaped $[GeN_2]^{4-}$.[13,17,20,21,23] But, none was observed in the planar triangular coordination before.

The Ge-N bond length of 1.786(8) Å in $Ba_9Ge_3N_{10}$ is shorter than any known Ge-N bonds by more than 0.1 Å. Ge-N bond lengths range from 1.84 to 1.95 Å [both in Ge(II), or Ge(IV)], and no Ge-N bond was observed below 1.83 Å in any known Ge-containing nitrides.[13,15,20-25] In a given coordination sphere, Ge-N bonds in shorter range around 1.84 Å are counterbalanced by much longer Ge-N bonds (1.9-2.1 Å) with no exception. By considering all three bond lengths in a given coordination sphere are 1.786(8) Å, shortening of the Ge-N bonds in $Ba_9Ge_3N_{10}$ is significant.

Triangular anion of $[GeN_3]^{5-}$ in $Ba_9Ge_3N_{10}$ provides an interesting example for the application of the valance bond model to a component of solid. Those unique structural features above suggest that the bonding configuration in $[GeN_3]^{5-}$ is analogous to that in well-known planar tri-

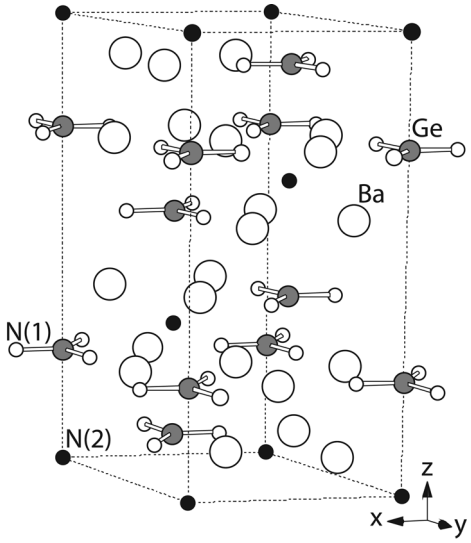

Figure 1. Unit-cell structure of $Ba_9Ge_3N_{10}$. Shaded circles are Ge. Large open circles are Ba. Nitrogens in different crystallographic sites are visually separated. N(1) or N(2) are designated as small open circles or small closed cicles, respectively. Small closed cicles [N(2)] are 1/3-occupied.

angular anion of NO_3^{-1}. Major difference between those two anions is that the expanded octet is allowed for Ge (empty 4d orbitals are available), whereas it is not for N. Unlike in NO_3^{-1}, where only one possible Lewis structure can be deduced, there are three different possible Lewis structures for the $[GeN_3]^{5-}$. All three possible Lewis structures indicate partial multiple-bonding character of Ge-N bonds. Considering Ge is more electropositive than N, it is suggested that the most stable structure is the one with Ge in formal charge of zero, which is shown in Figure 2. The resonance structure indicates 2 electrons are delocalized through π-interaction over 4 atoms, which conforms to the perfect feature of planar triangular shape. Symmetry consideration on point group D_{3h} suggests that P_z (A_2"), d_{xz} (E"), d_{yz} (E") orbitals in Ge are involved exclusively in the π-interaction. The partial multiple-bonding character of Ge-N bonds conforms to the observation of shortened lengths of Ge-N bonds.

The structure of a nitride crystal is interpreted in a specific way, often to emphasize certain aspect of the structure. Metal-centered polyhedral perspective is more often adopted to interpret the structures of the crystals than N-centered polyhedral one. The crystal structure can also be constructed

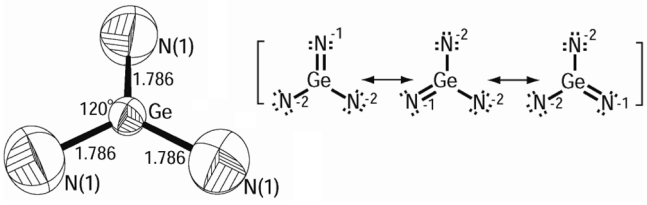

Figure 2. Coordination around Ge, which generates the symmetric planar triangular anion of $[GeN_3]^{5-}$. This anionic subunit is isostructural with NO_3^{1-}. Lewis structures are illustrated for the anion of $[GeN_3]^{5-}$.

from a hypothetical structural building block, by stacking it in a certain regular manner. In this case, the building block doesn't necessarily coincide with the crystallographic unit-cell. Such practice has been demonstrated in interpretations of the crystal structures of a few nitride compounds, such as Sr_3GaN_3, Sr_6GaN_5, $LiSrGaN_2$, $Li_4Sr_3Ge_2N_6$, Sr_3GeMgN_4, and β-Sr_2GeN_2.[21-23,26,37] In those examples, building blocks were constructed by N-centered polyhedral perspective, leading to an alternative interpretation of the crystal structure. Sometimes, such practice provides an interesting insight, which may not be obtained by usual interpretation.

Depending on how one rearranges the empirical formula, various different perspectives can be conceived. By conventional metal-centered polyhedral perspective, the empirical formula of $Ba_9Ge_3N_{10}$, can be rearranged into $[Ge_3N_9]^{15-}$ $[Ba_9N]^{15+}$, so that Ge-centered triangular anions are readily apparent. But configuration around N(2) sites is not straight forward because the sites are only partially occupied. Moreover, both Ge-centered and N-centered polyhedral perspectives had to be introduced together, in order to fully describe the overall structure. As an another variation, the empirical formula of $Ba_9Ge_3N_{10}$ can be rearranged into $[Ba_9Ge_3N_9]^{3+}N^{3-}$, a combination of N^{3-} anion with the cationic framework of $[Ba_9Ge_3N_9]^{3+}$. If we adopt N-centered polyhedral perspective, description of the overall structure can be made. Figure 3a shows the coordination sphere around N(1) in $Ba_9Ge_3N_{10}$, seen through N-centered polyhedral perspective. In most nitrides, N is six-coordinated to surrounding metals. Likewise, N coordinates to 5 × Ba and 1 × Ge, into a distorted octahedron of $[Ba_5GeN]^{11+}$. By sharing apical Ge, three of these octahedra combine into a hypothetical structural building block of $[Ba_{12}GeN_3]^{19+}$, as shown in Figure 3b and 3c. When looked parallel to [001], it appears as a triangular shape. This triangular building block contains $[GeN_3]^{5-}$ anion in the middle, which is then surrounded by 12 × Ba^{2+}.

By stacking these building blocks in a regular manner, overall structure of cationic framework of $[Ba_9Ge_3N_9]^{3+}$ can be constructed, as summarily shown in Figure 4. Connecting those triangular building blocks along xy-plane generates a layer of 2D-sheet, as in Figure 4a (layer A). Flipping over

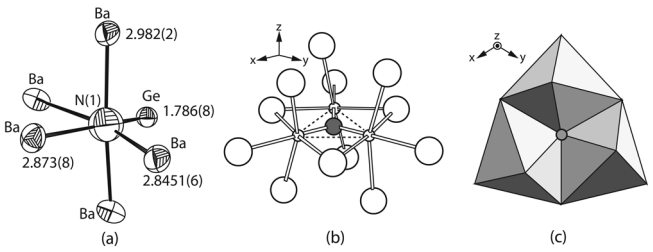

Figure 3. (a) Coordination around N(1), which generates the distorted octahedron of $[Ba_5GeN]^{11+}$. (b) Hypothetical building block of $[Ba_{12}GeN_3]^{19+}$, which is defined by merging three of those distorted octahedra in such a manner that Ge is in the center *via* edge-sharing. (c) The hypothetical building block has triangular shape, which is isostructural with the hypothetical building block of $[Sr_{12}GaN_3]^{18+}$, which was introduced in describing the crystal structure of Sr_3GaN_3.[26]

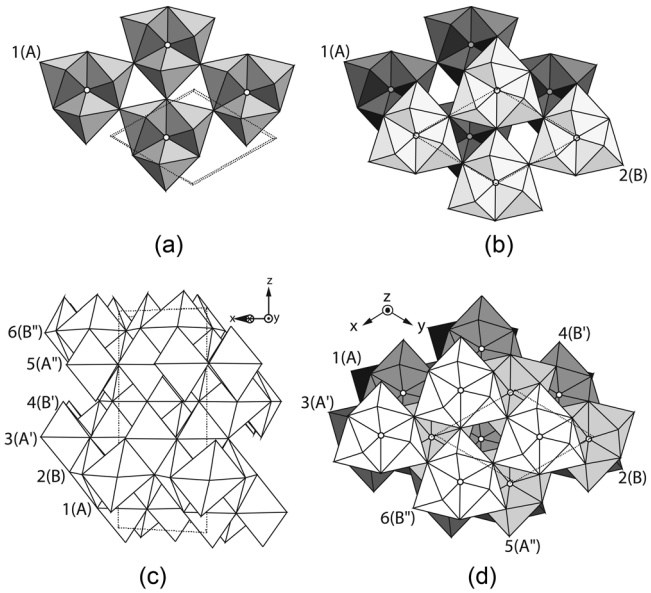

Figure 4. The structure of $Ba_9Ge_3N_{10}$ can be conceived as the cationic framework of $[Ba_9Ge_3N_9]^{3+}$ combined with N^{3-} anion. Polyhedral representation of $[Ba_9Ge_3N_9]^{3+}$ can be obtained by stacking those building blocks (in Figure 3c) in a regular manner. (a) A 2D-sheet (layer A) generated by putting the building blocks side by side along xy-plane. (b) Second sheet, layer B, is obtained by flipping the layer A, and is laid on top of the layer A. Ge of the layer B is placed over the middle of three Ge in the layer underneath. (c) Side view (along y-axis), and (d) the view along z-axis of the polyhedral representation of the cationic framework of $[Ba_9Ge_3N_9]^{3+}$. Stacking manner is represented by ⋯ABA'B'-A"B"ABA'B'A"B"⋯.

the first layer generates second sheet (layer B), which is then laid on top of the first layer so that each Ge in the second layer sits above the middle of the three Ge in the first one, as in Figure 4b (layer B on the layer A). Over the layer B, the layer A' is laid, so that Ge is placed over the center of the three Ge in the layer B, but not over the Ge in the layer A. The layer A' is obtained by 1/3-translation of layer A along the direction [1, −1, 0]. If stacking is repeated by this way, along c-axis, stacking fashion becomes ⋯ABA'B'A"B"ABA'B'A"B"⋯. A part of the overall crystal structure constructed by stacking the building blocks in such fashion is shown in Figure 4c (side view) and 4d (view from above). Stacking of a layer over another is accomplished by an extensive edge-sharing of those building blocks. Each Ba is shared by four different building blocks, two in the layer, one from the layer above, and the one from the layer below. Thus, the empirical formula of the cationic framework becomes $[Ba_{12/4}GeN_3]^{1+}$, which is same as $[Ba_9Ge_3N_9]^{3+}$.

Seen along the z-axis in Figure 4d, empty interstitial sites [N(2) sites] are apparent in the cationic framework of $[Ba_9Ge_3N_9]^{3+}$. The site is surrounded by 6 × Ba^{2+} which belong to four consecutive layers (designated as ABA'B' in the Figure 5). By introducing N^{3-} anions into these sites, overall crystal structure of $Ba_9Ge_3N_{10}$ will be completed. Only one third of the sites are occupied by N. N(2) coordinates to six surrounding Ba^{2+}, into an octahedral conformation shown in Figure 5. It is interesting to note that this

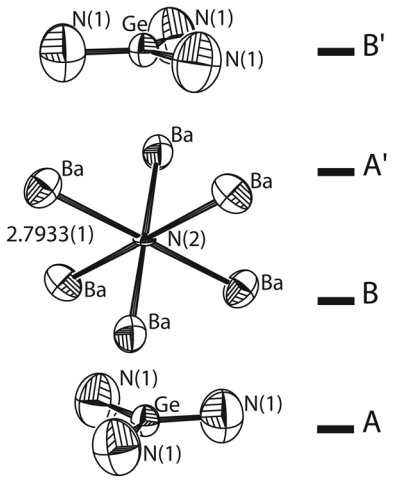

Figure 5. Coordination around N(2), which generates the octahedral subunit of $[Ba_6N]$. All six Ba-N bonds have same length, and Ba-N-Ba angles for pairs of opposing Ba are all 180 degree. ABA'B' designates where the stacking layers are.

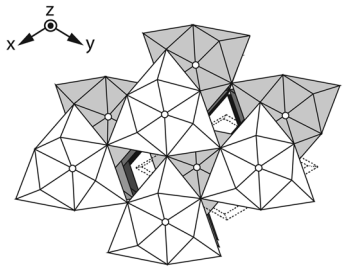

Figure 6. Polyhedral representation of Sr_3GaN_3, constructed from the hypothetical building block of $[Sr_{12}GaN_3]^{18+}$. Stacking of 2D-layers along z-axis was carried out in an alternating fashion of ⋯ ABABAB ⋯. Polyhedral representation of $Ba_9Ge_3N_{10}$ can be obtained by pushing the top of the stacked column from the side, toward [1, −1, 0] direction. Each layer will slide against others toward the direction, giving the polyhedral representation of the cationic framework of $[Ba_9Ge_3N_9]^{3+}$ shown in Figure 4d.

octahedral subunit of $[Ba_6N]$ has highly symmetric features. All 6 Ba-N bonds have identical bond length of 2.7933(1) Å, and Ba-N(2)-Ba bond angles for pairs of opposing Ba are all 180 degrees. Ba-N(2)-Ba bond angles for pairs of adjacent Ba are all near 90 degree [84.190(3) and 95.810(3)]. These symmetric features allude to the ionic character of the interaction between the cationic framework of $[Ba_9Ge_3N_9]^{3+}$ and N^{3-}.

The cationic framework of $[Ba_9Ge_3N_9]^{3+}$ shares the characteristic structural feature already seen in the structure of Sr_3GaN_3.[26] Figure 6 shows how the crystal structure of Sr_3GaN_3 can be constructed from the hypothetical structural building block of $[Sr_{12}GaN_3]^{18+}$, which has basically same conformation with $[Ba_{12}GeN_3]^{19+}$ shown in Figure 3c.[26] Unlike in $[Ba_9Ge_3N_9]^{3+}$, stacking of 2D-layers along c-axis was carried out in an alternating fashion of ⋯ABABAB⋯ in Sr_3GaN_3 (compare Figure 4d and Figure 6). As a result, unit-cell dimension of $Ba_9Ge_3N_{10}$ along c-axis is expected to be roughly three-fold that of Sr_3GaN_3, which is exactly what was observed (17.28 vs 5.41 Å). If top of the stacked column of Sr_3GaN_3 were pushed from side, along [1, −1, 0] direction, so that each layer slides against others toward the direction, one would get the structure of $[Ba_9Ge_3N_9]^{3+}$. It is readily obvious that the crystal structure of $Ba_9Ge_3N_{10}$ is closely related to that of Sr_3GaN_3. This example shows that, in some metal nitrides, N-centered polyhedral perspective could provide highly valuable structural information, which might not readily available from the conventional one.

As summary, $Ba_9Ge_3N_{10}$ contains isolated planar triangular anions of $[GeN_3]^{5-}$. The anion is isostructural with NO_3^{1-}. Ge has never been observed in such coordination sphere in any other known Ge-containing nitride compounds. Substantially shortened bond length of 1.786(8) Å suggests partial multiple bonding character of the Ge-N bonds, as can be expected from valence bond model. Each anion is surrounded by 12 cations of Ba^{2+}. The crystal structure of $Ba_9Ge_3N_{10}$ can be conceived as the cationic framework of $[Ba_9Ge_3N_9]^{3+}$, whose 1/3 of octahedral interstitial sites are occupied by N^{3-} anions. The way of constructing the structure for the cationic framework of $[Ba_9Ge_3N_9]^{3+}$, is closely related to that for the structure of Sr_3GaN_3. The coordination environment around Ge in $Ba_9Ge_3N_{10}$ is more close to that of Sr_3GaN_3, than any other known Ge-containing nitrides.

Supplementary Material. Supplementary material has been sent to Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (*crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html*), as CSD No. 419700, and can be obtained by contacting the FIZ and quoting the article details and the corresponding CSD number.

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