

Synthesis and Structure of a Second Polymorph of Strontium Germanium Nitride: β - Sr_2GeN_2

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A new ternary strontium germanium nitride, β - Sr_2GeN_2 , was obtained as single crystal from constituent elements in molten Na. It crystallizes in space group Cmca (No. 64) with $a = 5.441(1)$ Å, $b = 11.377(2)$ Å, $c = 12.229(2)$ Å, and $Z = 8$. Its crystal structure is closely related to that of polymorphic companion, α - Sr_2GeN_2 , both of which contain isolated bent anions of GeN_2^{4-} .

Key Words : Strontium germanium nitride, Polymorph, Crystal structure

Introduction

A range of many new ternary and quaternary nitrides have been synthesized in recent years.¹⁻¹⁰ Particularly, many new ternary nitrides with interesting structures and properties have been obtained by using Na as a molten solvent.¹¹⁻²⁰ In most cases, products contain nitridometallate anions whose charge is counterbalanced by alkaline earth cations, which were added to enhance solubility of nitrogen in the Na melt.

Known alkaline earth germanium nitrides contain either tetrahedral or angular nitridogermanate anionic units. Ca_4GeN_4 contains isolated tetrahedral anions of $[\text{GeN}_4]$, and $\text{Ca}_2\text{Ge}_2\text{N}_6$ has infinite chains of corner-shared $[\text{GeN}_4]$.¹³ Most of the known ternary germanium nitrides, such as $\text{Ba}_3\text{Ge}_2\text{N}_6$,²⁰ Ba_2GeGaN ,¹⁵ Ca_2GeN_2 ,¹³ $\text{Sr}_3\text{Ge}_2\text{N}_6$,¹⁷ or Sr_2GeN_2 ,¹⁷ contain 'dumbbell-shaped' bent GeN_2^{4-} anions. In this study we report structure of β - Sr_2GeN_2 , a new polymorph of Sr_2GeN_2 , both of which contain bent GeN_2^{4-} anions.

Experimentals

A Nb container was made by welding closed one end of Nb tubing (110 mm long, 9.5 mm od and 1 mm thickness) in an argon atmosphere, using a Centorr Associates arc furnace. Under argon in a VAC dry-box, NaN_3 (58.1 mg, Aldrich, 99%), Na (147 mg, Aldrich, 99%), Ge (51.2 mg, Cerac, 99.999%), Sr (123.4 mg, Aldrich, 99%), and Mg (17.6 mg, Aldrich, 99.98%) were loaded in the Nb container, and other end was subsequently welded closed. In order to protect the container from oxidation, it was put into silica tubing and sealed under vacuum. The molar ratio of Na : Ge : Sr : Mg was 10 : 1 : 2 : 1. 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. Thereafter, the furnace was turned off. The solid products

(crystals) were retrieved from the container after Na was separated from them by sublimation at 300 °C under a dynamic vacuum.

A single crystal of β - Sr_2GeN_2 was mounted in a drop of poly(butene) oil sustained in a plastic loop. A flow of cold nitrogen gas over the sample solidified the oil, and protected the sample from contact with air. X-ray diffraction data were collected with a Bruker SMART system with a CCD detector (40 mm distance). Over 180 degree range 600 frames of data were collected for omega and phi, respectively. The SAINT software was used for integration of the diffraction data.²¹ An empirical absorption correction was applied using SADABS.²² The structure was solved by the direct method, using SHELXS.²³ Refinement of the structure was carried out by the full-matrix least square method (on F^2), using SHELXL.²³ The atomic parameters were standardized by using STRUCTURE TIDY.²⁴ The space group was verified by using ADDSYM.²⁵ WDX (wavelength dispersive X-ray) and semi-quantitative (without a standard) EDX (energy dispersive X-ray) analysis were carried out using a JEOL JXA-8900R WD/ED combined microanalyzer.

Results and Discussion

The product was obtained as a black powder. Under a microscope, the powder was shown to be a mixture of three different types of single crystals; transparent yellow, transparent clear with a brownish tint, and black. When exposed to air, those crystals readily decompose and produce NH_3 , indicating they are nitrides. In poly(butene) oil, they could be handled for a few days without any significant degradation. Structural analysis of the transparent clear crystals with a brownish tint was unsuccessful. The characterization of the yellow crystals showed that it is a new quaternary nitride containing Mg: $\text{Sr}_3\text{GeMgN}_4$.²⁶

The black crystals had a rectangular prismatic shape. Those black crystals were composed of two different kinds, which were visibly discernible under microscope. A portion of the black crystals had a non-reflecting dull surface. Under a microscope, line patterns on the dull surface could be seen,

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running along one specific direction (the [010] direction). In contrast, the remaining black ones had a smooth surface, which gives blue perception by reflecting light. EDX analysis on a few crystals indicated that the chemical compositions of these two different black crystals are same within error. The Sr:Ge ratio of the black crystals was close to 2 : 1 ($65:35 \pm 3\%$; decomposition slowly occurred in the e-beam). No Na or Mg was detected by the EDX analysis, and N was qualitatively identified by WDX analysis. Indexing the single crystal diffraction peaks indicated the black crystals with the blue-reflecting smooth surface is the known, Sr_2GeN_2 ,¹⁷ whereas, that with the dull surface turned out to be a new polymorph of the same composition. The new crystal has unit cell volume of 756.9 \AA^3 , which is very close to that of the known Sr_2GeN_2 (749.7 \AA^3).¹⁷ Whereas the known Sr_2GeN_2 (hereafter $\alpha\text{-Sr}_2\text{GeN}_2$) belongs to the tetragonal system ($a = 11.773$, $c = 5.409 \text{ \AA}$),¹⁷ the new crystal belongs to the orthorhombic with unit cell parameters ($a = 5.441$, $b = 11.377$, and $c = 12.229 \text{ \AA}$).

Systematic extinctions suggested the space group Cmca. A starting structural model was obtained for the heavy atoms (Sr and Ge) by the direct method in Cmca. N1 and N2 were located in the early stages of the refinement of the starting model. The final refinement was obtained with $R_1 = 3.8\%$. Crystallographic data are provided in Table 1 through 4.

Figure 1 shows the structure of $\beta\text{-Sr}_2\text{GeN}_2$. It contains isolated angular nitridogermanate anions, GeN_2^{4-} , stacked along a-axis. Sr are located in between those GeN_2^{4-} units.

Table 1. Crystallographic data for $\beta\text{-Sr}_2\text{GeN}_2$

Crystal system	Orthorhombic
Space group	Cmca (No. 64)
a / \AA	5.441(1)
b / \AA	11.376(2)
c / \AA	12.229(2)
V / \AA^3	756.9(3) \AA^3
Z	8
D (calcd) / g cm^{-3}	4.841
T / K	173(2)
Formula weight	275.85
Wavelength / \AA	0.71073
Abs. Coeff. / mm^{-1}	35.7
F(000)	976
Crystal size / mm^3	0.1 \times 0.08 \times 0.02
θ / degree	3.33 to 31.55
Index ranges	$-7 \leq h \leq 6$, $-15 \leq k \leq 16$, $-17 \leq l \leq 12$
Refln. collected	2414
Independent refln.	644 [R(int) = 0.0577]
Data / restraints / parameters	644 / 0 / 32
Goodness-of-fit on F^2	1.094
Final R indices [$I > 2\sigma(I)$] ^a	R1 = 0.0303, wR2 = 0.0605
R indices (all data)	R1 = 0.0381, wR2 = 0.0629
Extinction coefficient	0.00092(19)
Largest diff. peak and hole	1.204 and $-1.403 \text{ e.\AA}^{-3}$

^a $R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$, $wR2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^2)^2]}{2}$, where $w = 1/[\sigma(F_o^2)^2 + (gP)^2 + jP]$, $P = [\max(F_o^2, 0) - 2F_c^2]/3$, $g = 0.0282$, $j = 3.0758$.

Table 2. Atomic coordinates ($\times 10^{-4}$) and equivalent isotopic displacement parameters for $\beta\text{-Sr}_2\text{GeN}_2$

atom	sites	x	y	z	U_{eq}^a
Sr(1)	8f	0	479(1)	3576(1)	5(1)
Sr(2)	8f	0	3564(1)	4411(1)	5(1)
Ge(1)	8f	0	2398(1)	1799(1)	6(1)
N(1)	8f	0	797(4)	1419(4)	6(1)
N(2)	8f	0	3389(5)	597(4)	8(1)

^aThe equivalent isotropic thermal displacement parameter, U_{eq} in $\text{\AA}^2 \times 10^{-3}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for $\beta\text{-Sr}_2\text{GeN}_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + 2 h k a^* b^* U_{12} + \dots]$

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

Table 4. Selected interatomic spacings [\AA] and bond angles [degree] in $\beta\text{-Sr}_2\text{GeN}_2$

(GeN ₂ ⁴⁻ unit)			
	N1-Ge-N2		113.2(2)
(N1-centered distorted octahedron)			
N1-Ge	1.879(5)	Sr2-N1-Sr2	84.7(2)
N1-Sr1	2.662(5)	Ge-N1-Sr1	83.5(2)
N1-Sr1	2.744(1)	Ge-N1-Sr1	97.3(1)
N1-Sr2	2.561(5)	Ge-N1-Sr2	87.8(2)
N1-Sr2	2.737(5)	Sr2-N1-Sr1	104.0(2)
		N1-Sr2-N1	95.3(2)
(N2-centered distorted octahedron)			
N2-Ge	1.852(5)	Sr1-N2-Sr1	85.5(2)
N2-Sr2	2.653(5)	Ge-N2-Sr2	85.7(2)
N2-Sr2	2.728(1)	Ge-N2-Sr2	92.7(1)
N2-Sr1	2.584(5)	Ge-N2-Sr1	104.5(2)
N2-Sr1	2.787(5)	Sr2-N2-Sr1	84.4(2)
		N2-Sr1-N2	94.5(2)
(Sr1-centered distorted square pyramid)			
Sr1-N2 ^a	2.584(5)	N2 ^a -Sr1-N1	120.8(2)
Sr1-N2	2.787(5)	N2 ^a -Sr1-N1	96.9(1)
Sr1-N1	2.662(5)	N2 ^a -Sr1-N2	94.5(2)
Sr1-N1	2.744(1)	N1-Sr1-N1	89.1(1)
		N1-Sr1-N2	86.4(1)
		N1-Sr1-N1	164.9(2)
		N1-Sr1-N2	144.7(2)
(Sr2-centered distorted square pyramid)			
Sr2-N1 ^a	2.561(5)	N1 ^a -Sr2-N1	95.3(2)
Sr2-N1	2.737(5)	N1 ^a -Sr2-N2	73.3(2)
Sr2-N2	2.653(5)	N1 ^a -Sr2-N2	91.4(1)
Sr2-N2	2.728(1)	N2-Sr2-N2	86.6(1)
		N2-Sr2-N1	93.8(1)
		N2-Sr2-N2	171.6(2)
		N2-Sr2-N1	168.6(2)

^aapical N of the square pyramid

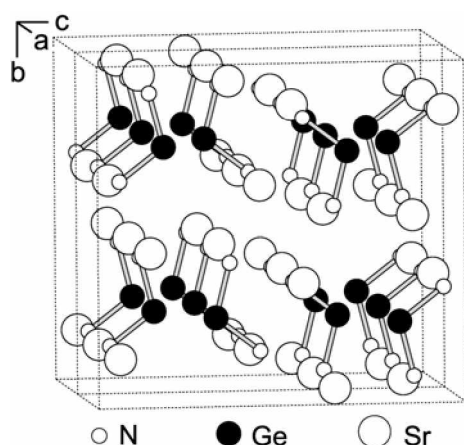


Figure 1. Structure of β - Sr_2GeN_2 . Only Ge-N bonds are shown to depict the bent units of GeN_2^+ .

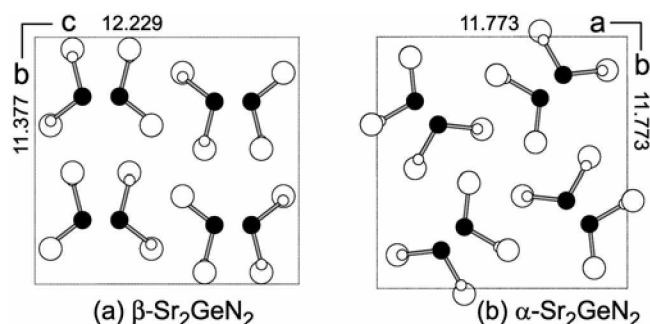


Figure 2. (a) Structure of β - Sr_2GeN_2 , viewed along the *a*-axis (the shortest axis). (b) Structure of α - Sr_2GeN_2 , viewed along the tetragonal axis. Only Ge-N bonds are shown to depict the bent units of GeN_2^+ . Lattice parameters (in Å) are shown along the unit cell outlines.

The Ge-N bond lengths are slightly different, 1.852 and 1.879 Å, and the N-Ge-N bond angle is 113.2° , which are almost identical to those of the known Sr_2GeN_2 (Ge-N=1.85 and 1.88 Å, N-Ge-N= 113.6°).¹⁷ Other bond lengths and angles of β - Sr_2GeN_2 listed in Table 4 are also very close to those of Sr_2GeN_2 . Therefore, it appears that these two polymorphs have almost identical local environments, even though they are different in overall structure. In order to see what differentiates these two compounds, their crystal structures are compared in Figure 2. It is apparent that structural

difference originates from the relative orientation of the GeN_2^+ units. The 'dumbbell-shaped' bent units are aligned in a linear pattern in β - Sr_2GeN_2 , whereas they have a rotary "alignment" around the 4-fold axis in α - Sr_2GeN_2 .

N-centered polyhedral perspective provides an alternative way to see how these subtle difference of the relative orientation can be understood. It is often instructive to view the structure of nitrides as condensed N-centered polyhedral units. The utility of such a view has been well demonstrated in the interpretation of the structure of subnitrides, such as NaBa_3N , $\text{Na}_5\text{Ba}_3\text{N}$ (both, one-dimensional extended structure),^{27,28} $\text{Ca}_4\text{In}_2\text{N}$ (two-dimensional),²⁹ or Ca_3AuN (three-dimensional).³⁰ The practice has also been applied to the interpretation of the structures of nitrides, such as $\text{Sr}_3\text{Ga}_2\text{N}_3$, $\text{Sr}_6\text{Ga}_2\text{N}_3$,³¹ $\text{LiSrGa}_2\text{N}_3$,³² or $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$,³³ and provided an interesting way to understand the structural features of those nitrides. In the first four of the above ternary metal nitrides, N is six-coordinate to surrounding metals, which generate a distorted octahedral unit of $[\text{AE}_6\text{N}]$ (AE=Ca, Sr, or Ba). It has been suggested that the solubility of N in a Na melt is enhanced by adding an alkaline earth to form $[\text{AE}_6\text{N}]$ ($[\text{Sr}_6\text{N}]$ in this study).^{27,28} When M (M=metal other than alkaline earth) is also introduced to the melt, AE_5MN may be formed. Such unit has been observed in a few ternary nitrides, as for example in Ba_5ZnN_2 (unit of $[\text{Ba}_5\text{ZnN}]$),¹² or $\text{Sr}_3\text{Ga}_2\text{N}_3$ (unit of $[\text{Sr}_3\text{Ga}_2\text{N}]$).³¹ Replacing a Sr with a Ge in $[\text{Sr}_6\text{N}]$ will generate $[\text{Sr}_5\text{GeN}]$, and two of those can condense into hypothetical structural units of $[\text{Sr}_8\text{Ge}_2\text{N}_2]$, which are shown in Figure 3 for N1- or N2-centered pseudo-octahedra. By further condensing these units via sharing their edges and corners, a two-dimensional extended structure (a sheet in Figure 4) can be constructed. Then, by stacking these sheets in ordered manner, three-dimensional structures of β - Sr_2GeN_2 or α - Sr_2GeN_2 can be constructed (Figure 4). In both cases, stacking was carried out in alternating manner (. . AAAAAA . .). In so doing, it becomes apparent that the relative placement of adjacent sheets is a critical factor in differentiating the overall structure. In β - Sr_2GeN_2 , adjacent sheets are related by a translation along the *b*-axis of $1/2b$, whereas they are related by a 90° rotation in α - Sr_2GeN_2 . If a slight adjustment of the bond lengths and angles in the pseudo-octahedral units are introduced during such hypothetical stacking, we can

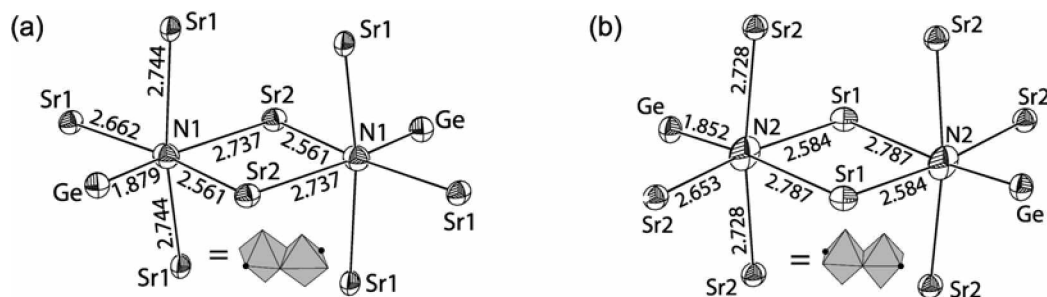


Figure 3. A structural unit of $[\text{Sr}_8\text{Ge}_2\text{N}_2]$, which is used as the hypothetical structural unit in a polyhedral perspective. (a) Coordination around N1-centered distorted octahedron. (b) Coordination around N2-centered distorted octahedron. The thermal ellipsoids are shown at 99% level.

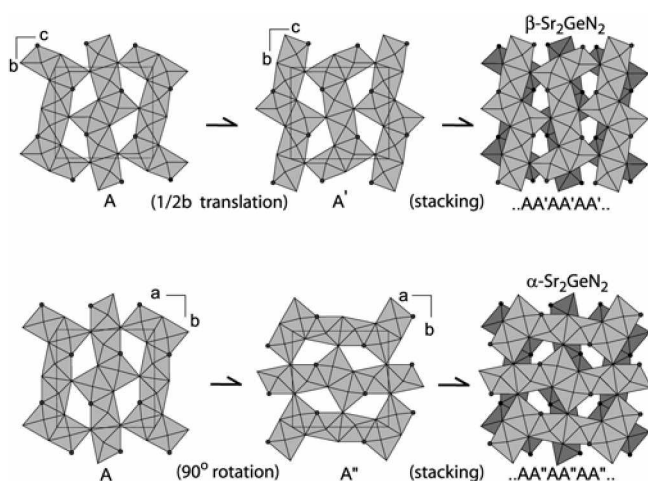


Figure 4. N-centered polyhedral perspective of the crystal structures of β - Sr_2GeN_2 and α - Sr_2GeN_2 . The structural features are built up via stepwise condensing of the hypothetical small polyhedral units.

rationalize how α - Sr_2GeN_2 belongs to the tetragonal system, while β - Sr_2GeN_2 belongs to the orthorhombic system. Small differences in the dimensions of the repeat unit of the sheet (rectangular unit-cell outline in Figure 4) can be accommodated when stacked after a 90° rotation (imagine a fat cross), whereas the differences may be preserved if stacking is carried out with a $1/2b$ -translation. Whether such hypothetical condensed units actually exist as individual fragments in the Na-melt or not is an open question. But, the N-centered polyhedral perspective in looking at the structure of nitrides provides a better understanding when these hypothetical condensed units are introduced. It is worth noting that both polymorphs coexist in a same batch, and Mg was present during the synthesis. Mg might have played a role in differentiating the details of single crystal growth. However, we did not previously observe the β -polymorph in previous syntheses where Mg was not included.

Empty space between the stacked sheets generates channels along the short axis (a-axis in β - Sr_2GeN_2). Figure 5a shows an array of GeN_2^{4+} units along the a-axis. The bent GeN_2^{4+} is isosteric to bent molecules of SO_2 or SnCl_2 , which have 18 valence electrons. Based on an sp^2 hybridized configuration, two of those valence electrons are a non-bonding electron pair, and it is suggested that the pair resides in the "empty" space. The distorted ellipsoid in Figure 5a between adjacent units depicts a relatively large vacant region, whose surrounding detail is shown in Figure 5b. Sr is coordinated to five N, generating a pseudo square pyramidal unit of $[\text{SrN}_5]$. The empty space is surrounded by two of these $[\text{SrN}_5]$ units (rectangular bases of the pyramids facing toward the space), and three GeN_2^{4+} units. Therefore, the nonbonding electron pair on Ge is surrounded by four metal near neighbors (Sr1, Sr2, and two adjacent Ge). The Ge-Ge distance between adjacent GeN_2^{4+} units is 3.215 Å, which is significantly longer than Ge-Ge single bond length (2.4–2.6 Å). The Ge-Sr2 distance is 3.458 Å. The Ge is much nearer to Sr1 (Ge-Sr1 distance 3.080 Å), probably indicating weak

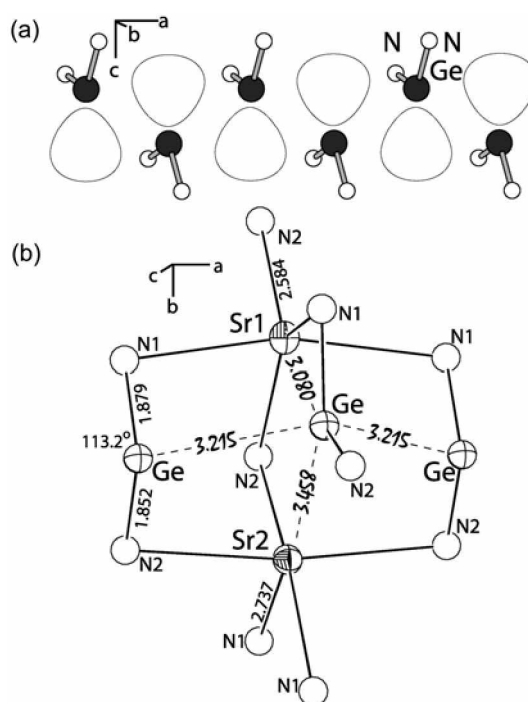


Figure 5. (a) An array of the GeN_2^{4+} units along a-axis in β - Sr_2GeN_2 . Distorted ellipsoids designate an empty space around the sp^2 position of Ge. (b) Local coordination around the vacant region around Ge.

coordination of the Sr to the lone pair, as seen in the previous example of $\text{Ba}_3\text{Ge}_3\text{N}_4$.²⁰ Direct evidence of the electron density in the region cannot be obtained by the diffraction method used in this study. But a common feature of angular GeN_2^{4+} units having a relatively large vacant region in one remaining sp^2 position also occurs in Ca_2GeN_3 ,¹³ Ba_3GeN_3 ,²⁰ $\text{Sr}_3\text{Ge}_2\text{N}_2$,¹⁷ α - Sr_2GeN_2 .¹⁷

Summary

A new strontium germanium nitride, β - Sr_2GeN_2 , contains isolated bent units of GeN_2^{4+} . The crystal structure is very similar to that of its polymorphic companion, α - Sr_2GeN_2 . The values of the bond lengths and angles of β - Sr_2GeN_2 are very close to those of α - Sr_2GeN_2 . Locally, the large vacant region around sp^2 position of Ge in β - Sr_2GeN_2 has an identical environment to the one in α - Sr_2GeN_2 , which suggests a stereochemically active lone pair of electrons on the Ge. A differentiating factor of the crystal structures of those two polymorphs is the relative orientation of the GeN_2^{4+} units in the lattice. The N-centered polyhedral perspective provides an interesting way to interpret these structural features.

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