

Synthesis and Crystal Structure of the New Quaternary Subnitride, Sr₂GeGaN.

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Recently, the number of Ge- or Ga- containing nitride compounds synthesized in Na melt has grown rapidly.¹⁻¹⁸ But, the example of nitride compound containing both Ge and Ga is rare. Our synthetic efforts of getting such nitrides instead gave a new quaternary subnitride, Sr₂GeGaN, which is isostructural to its Ba analogue,⁶ Ba₂GeGaN. Crystallographic data on Sr₂GeGaN are provided in Table 1-3. The crystal structure of Sr₂GeGaN is given in Figure 1. The structure of intermetallic SrGe¹⁹ is also provided in the figure for comparison.

A zigzag chain composed of alternating Ge and Ga runs along the b-axis through a channel generated by surrounding Sr, as seen in Figure 1a and 1b. Ga in the chain is bonded to N at a distance of 1.882(4) Å. It is interesting to note that the crystal structure of Sr₂GeGaN is closely related to that of SrGe.¹⁹ Figure 1c and 1d. It appears as if one [Ge] in intermetallic SrGe has been replaced by [GaN]. This observation suggests formal charge of +1 for Ga. The empirical formula, Sr₂GeGaN, can be rearranged into Sr₂[Ge]²⁺[GaN]²⁻, which conforms to

the replacement of half of [Ge]²⁺ in SrGe by [GaN]²⁻. The valences and Madelung potentials calculated for each atom, which were provided in Table 4, conform to this assignment. Typically, the potential for any site is -10 V times the ionic charge.²⁰

As in SrGe, [GaN]²⁻ or [Ge]²⁺ is surrounded by the mono-capped trigonal prism of 7 × Sr. The mono-capped trigonal prisms of 7 × Sr stack along b-axis via sharing their rectangular side faces, thereby, generating the conduit through which the zig-zag chain passes through. The channel has roughly hexagonal shape when looked through the b-axis (Figure 1a), but is severely distorted, when compared to that in SrGe (Figure 1c). Because of the distortion, the unitcell of Sr₂GeGaN adopts monoclinic system rather than more symmetric tetragonal one observed for SrGe. It is apparent that the replacement of [Ge] into [GaN] in the Ge-Ge chain lowers the symmetry of the overall crystal structure.

Ga-Ge bond length is 2.447(1) Å, which is shorter than Ga-Ge distance of 2.508(2) Å in its Ba analogue,⁶ Ba₂GeGaN. It is significantly shorter than Ge-Ge bond length, of 2.634 Å in SrGe,¹⁹ and is also shorter than any known Ge-Ge distances in

Table 1. Crystallographic data for Sr₂GeGaN.

Crystal system	Monoclinic
Space group	P2 ₁ /m
Unit cell dimensions	a = 6.885(1) Å b = 4.0432(6) Å c = 8.680(2) Å β = 108.454(8)°
Volume (Å ³)	229.21(6)
Z	2
Density (calcd/ mg m ⁻³)	4.804
Absorption coefficient (mm ⁻¹)	35.252
Temperature (K)	173(2)
F(000)	292
Crystal size (mm ³)	0.100 × 0.025 × 0.025
θ range for data collection (°)	2.47 to 30.51
Index ranges	-8 ≤ h ≤ 9, -5 ≤ k ≤ 5, -12 ≤ l ≤ 12
Reflections collected	3617
Independent reflections	792 [R(int) = 0.0401]
Data / restraints / parameters	792 / 0 / 32
Goodness-of-fit on F ²	1.106
Final R indices [I > 2 sigma(I)] ^a	R1 = 0.0206, wR2 = 0.0451
R indices (all data) ^a	R1 = 0.0263, wR2 = 0.0458
Largest diff. peak and hole (e.Å ⁻³)	1.125 and -0.974

^aR1 = Σ|F_o - |F_c|| / Σ|F_o|, wR2 = [Σw(F_o² - F_c²)² / ΣwF_o²]^{1/2}, where w = 1 / [σ(F_o²) + (gP)² + jP], P = [max(F_o², 0) + 2F_c²] / 3, g = 0.0152, j = 0.0115.

Table 2. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for Sr₂GeGaN.

	Wyckoff	x	y	z	U(eq)
Sr(1)	2e	7978(1)	2500	339(1)	4(1)
Sr(2)	2e	8154(1)	2500	6218(1)	4(1)
Ge	2e	3241(1)	2500	7009(1)	4(1)
Ga	2e	4647(1)	2500	2481(1)	4(1)
N	2e	1767(6)	2500	1705(5)	5(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Anisotropic displacement parameters (Å² × 10³) for Sr₂GeGaN.

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Sr(1)	2(1)	5(1)	3(1)	0	1(1)	0
Sr(2)	4(1)	5(1)	3(1)	0	1(1)	0
Ge	3(1)	5(1)	5(1)	0	1(1)	0
Ga	2(1)	5(1)	5(1)	0	1(1)	0
N	4(2)	6(2)	5(2)	0	1(2)	0

The anisotropic displacement factor exponent takes the form: -2π² [h²a²U₁₁ + ... + 2hka'b'U₁₂].

one dimensional Ge^{2-} zig-zag chains found in ternary nitrides. The Ge-Ge bond length in the Ge^{2-} chain is 2.451(4), 2.5445(7), 2.500(1), and 2.5873(9) Å, for $\text{Sr}_3\text{Ge}_2\text{N}_2$,⁸ $\text{Sr}_6\text{Ge}_3\text{N}_2$,¹¹ $\text{Ba}_3\text{Ge}_2\text{N}_2$,¹¹ and $\text{Ba}_6\text{Ge}_3\text{N}_2$,¹⁴ respectively. The interatomic separation in elemental Ga or elemental Ge is 2.71, or 2.74 Å,²¹ respectively.

In most cases, crystal structures of metal nitrides are interpreted by visualizing them through cation(metal)-centered polyhedral perspective. This practice provides better view on polyhedral anionic components of nitridometallates, such as triangular $[\text{GeN}_3]^{5-}$,²² tetrahedral $[\text{GeN}_4]^{8-}$,⁴ dumbbell-shaped $[\text{GeN}_2]^{4-}$,^{4,8,11,13} or 'bow tie' unit of $[\text{Ge}_2\text{N}_6]^{16-}$.¹⁵ It also clarifies the connectivity among these nitridometallate units. But, in the case of subnitrides, Ba_2GeGaN or Sr_2GeGaN , the conven-

tional cation-centered polyhedral perspective provides neither any appreciable structural characteristics, nor any space-filling model. Once the formal charges of the elements were deduced in a reasonable manner (see above), anion-centered polyhedral perspective may be useful in envisioning the structure from another viewpoint. In many cases, anion-centered polyhedral perspective also provided interesting aspects of the crystal structure, especially by visualizing space-filling building blocks. Such practice of getting interesting information by applying anion-centered polyhedral perspective was well demonstrated in some of our previously reported nitrides, such as in Sr_2GeN_2 ,¹³ $\text{Sr}_6\text{Ge}_3\text{N}_2$,¹⁴ $\text{Li}_3\text{Sr}_3\text{Ge}_2\text{N}_6$,¹⁵ or $\text{Sr}_3\text{GeMgN}_4$.¹⁶

Figure 2a and 2b show the coordination spheres around elements in negative formal charges. N^{3-} is coordinated to 6 cations ($5 \times \text{Sr}^{2+}$ and $1 \times \text{Ga}^{1+}$) into the pseudo-octahedron of $[\text{Sr}_5\text{GaN}]$ in Figure 2a. The octahedral coordination has been most commonly observed for N in other known metal nitride compounds.²⁻¹⁸ The bond lengths of Sr-N [2.501(4)-2.732(3) Å] are in the range of distances observed in other nitrides, and that of Ga-N [1.882(4) Å] is also similar to the ones in other nitrides. The coordination sphere around Ge^{2-} is crowdier than that around N^{3-} , alluding to the difference of ionic sizes between them. Ge^{2-} is coordinated to 9 cations ($7 \times \text{Sr}^{2+}$ and $2 \times \text{Ga}^{1+}$) into distorted tri-capped trigonal prism of $[\text{Sr}_7\text{Ga}_2\text{Ge}]$ (Figure 2b). As seen in Figure 1d, Ge^{2-} is coordinated to 7 ×

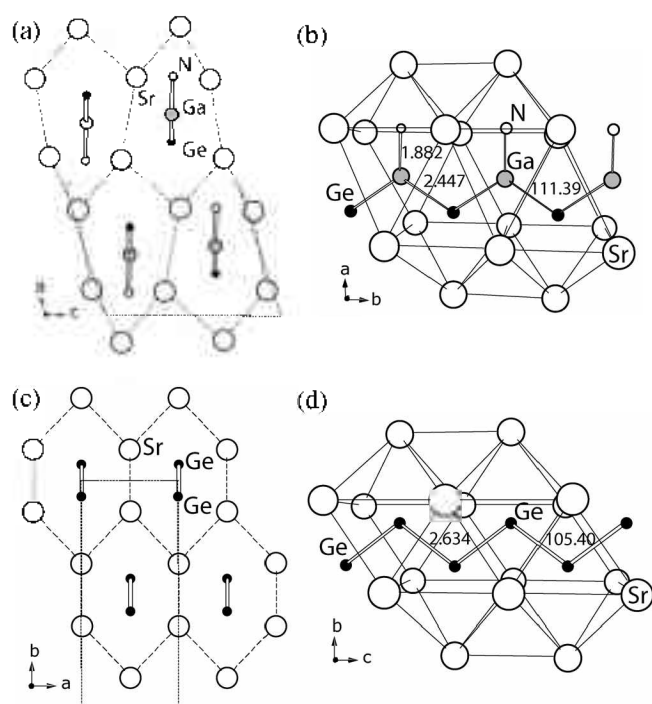


Figure 1. Comparison between crystal structures of Sr_2GeGaN and SrGe . (a) The structure of Sr_2GeGaN viewed along b-axis, and (b) along c-axis. (c) The structure of SrGe viewed along c-axis, and (d) along a-axis. Symmetric tetragonal unit-cell of SrGe is distorted into monoclinic one of Sr_2GeGaN , as $[\text{Ge}]^{2-}$ is replaced by $[\text{GaN}]^{2-}$.

Table 4. Bond valences and Madelung potentials from Eutax for Sr_2GeGaN .

Bond valences		
Sr(1) = 1.61	Sr(2) = 1.45	N = 2.46
Ga = 2.39	Ge = 2.99	
Madelung site potentials		
Atom	Pot(V)	Input charge
Sr(1)	-18.84	+2
Sr(2)	-16.11	+2
Ga	-14.12	+1
Ge	16.67	-2
N	26.32	-3

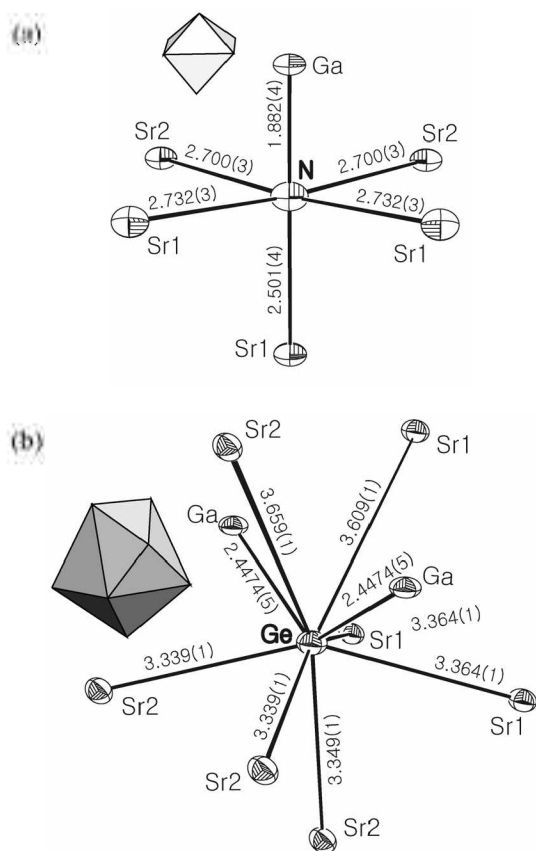


Figure 2. Coordinations around elements in negative formal charges. (a) N^{3-} coordinates to 6 × cations into octahedron of $[\text{Sr}_5\text{GaN}]$. (b) Ge^{2-} coordinates to 9 × cations into distorted tri-capped trigonal prism of $[\text{Sr}_7\text{Ga}_2\text{Ge}]$.

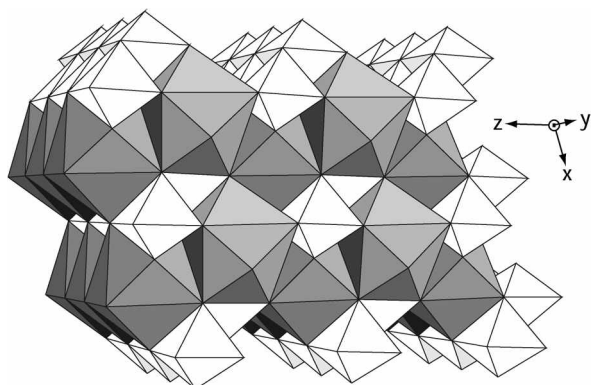


Figure 3. Polyhedral representation of the crystal structure of Sr_2GeGaN , constructed from the anion-centered polyhedral perspective. Polyhedral subunit in dark shade is tri-capped trigonal prism of $[\text{Sr}_2\text{Ga}_2\text{Ge}]$, and one in light shade is octahedron of $[\text{Sr}_2\text{GaN}]$, shown in Figure 2.

Sr^{2+} into mono-capped trigonal prism of $[\text{Sr}_2\text{Ge}]$ in SrGe . It is interesting to note that Ge^{2-} accommodates two more cations ($2 \times \text{Ga}^{1+}$) into its coordination sphere, when alternating $[\text{Ge}]^{2-}$ of SrGe is replaced by $[\text{GaN}]^{2-}$, turning it into Sr_2GeGaN . The bond lengths of Sr-Ge range from 3.3392(7) to 3.6586(8) Å. These tri-capped trigonal prisms of $[\text{Sr}_2\text{Ga}_2\text{Ge}]$ and octahedrons of $[\text{Sr}_2\text{GaN}]$ share their faces and edges into the space filling version of the crystal structure of Sr_2GeGaN , shown in Figure 3. One might conceive getting a new material such as SrGaN or BaGaN by replacing the remaining Ge^{2-} into $[\text{GaN}]^{2-}$. Such a material, SrGaN or BaGaN , is not yet known or obtained, and we couldn't get them within the extent of our efforts. But, it becomes obvious, from the anion-centered polyhedral perspective, that the remaining Ge in Sr_2GeGaN cannot be replaced by another set of $[\text{GaN}]$ without disrupting the current structural theme originated from SrGe . Only an analogue known to date is CaGaN ,²³ and as can be anticipated, its layered structure doesn't share any structural theme which can be traced back to Sr_2GeGaN or SrGe .

Experimental

Sr_2GeGaN was synthesized as single crystals from constituent elements in molten Na by the Na-flux method, as described in previous reports on other nitrides.¹²⁻¹⁸ Reactants used for the synthesis were NaN_3 (110.0 mg, Aldrich, 99%), Na (251 mg, Aldrich, 99%), Sr (87.9 mg, Aldrich, +99%), Ge (72.4 mg, Cerac, 99.999%), Ga (69.8 mg, Cerac, 99.999%), and Li (12.2 mg, Aldrich, 99.9%). The molar ratio of Na:Sr:Ge:Ga:Li was 13:1:1:1:0.5. Product was obtained as dark silvery powder, which readily decomposed when it was exposed in air. Poly(butene) oil was used to prevent decomposition in air during X-ray diffraction data collection. X-ray diffraction data were collected with a Bruker X8 APEX II diffractometer equipped with 4K CCD detector. Initial orientation matrix was obtained by using APEX2 program.²⁴ The integration of the diffraction data was carried out by the program SAINT.²⁵ An empirical absorption correction was applied using SADABS.²⁶ The initial input file for solving the crystal struc-

ture was prepared by XPREP.²⁷ The structure was solved by the direct method, using SHELXS.²⁸ Refinement of the structure was carried out by the full-matrix least square method (on F^2), using SHELXL.²⁸ The atomic parameters were standardized by using STRUCTURE TIDY.²⁹ The space group was verified by using ADDSYM.³⁰ Bond valence and Madelung potential was calculated by EUTAX.²⁰ 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.

Product was mainly a mixture of Ga_2Sr (silvery) and Sr_2GeGaN (black). Indexing on the single crystal diffraction peaks obtained from the black crystal indicated the crystal is a new compound, which belongs to monoclinic system, with unit-cell parameters of $a = 6.885(1)$, $b = 4.0432(6)$, $c = 8.680(2)$ Å, and $\beta = 108.454(8)^\circ$. 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 Sr, Ge and Ga were observed with no other ones related to Li or Na. The atomic ratio of Sr/Ge, Sr/Ga, and Ga/Ge were measured to be $1.93 (\pm 0.01)$, $2.0 (\pm 0.1)$, and $0.97 (\pm 0.04)$, respectively. Therefore, elemental ratio of Sr:Ge:Ga was 2:1:1.

Systematic extinctions in the diffraction data suggested the space group of $P2_1/m$. Initial structure solution was obtained by the direct method. Four crystallographic sites with substantial electron densities could immediately be allocated for Sr, Ge, and Ga. By including N into the solution, structural refinement reached the level of $R1 = 2.06\%$. The atomic ratio between Sr, Ge, and Ga was 2:1:1, which conforms to the value obtained by EDS analyses. The empirical formula came out to be Sr_2GeGaN .

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. 420413, and can be obtained by contacting the FIZ and quoting the article details and the corresponding CSD number.

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References

- Kowach, G. R.; Brese, N. E.; Bolle, U. M.; Warren, C. J.; DiSalvo, F. J. *J. Solid State Chem.* **2000**, *154*, 542.
- Yamane, H.; DiSalvo, F. J. *J. Solid State Chem.* **1995**, *119*, 375.
- Gal, Z. A.; Clarke, S. J. *Chem. Comm.* **2005**, 728.
- Clarke, S. J.; DiSalvo, F. J. *Inorg. Chem.* **2000**, *39*, 2631.
- Clarke, S. J.; DiSalvo, F. J. *J. Alloys Comp.* **1998**, *274*, 118.
- Clarke, S. J.; DiSalvo, F. J. *J. Alloys Comp.* **1997**, *259*, 158.
- Clarke, S. J.; DiSalvo, F. J. *Inorg. Chem.* **1997**, *36*, 1143.
- Clarke, S. J.; Kowach, G. R.; DiSalvo, F. J. *Inorg. Chem.* **1996**, *35*, 7009.
- Yamane, H.; DiSalvo, F. J. *Acta Cryst.* **1996**, *C52*, 760.
- Yamane, H.; DiSalvo, F. J. *J. Alloys Comp.* **1996**, *240*, 33.

11. Yamane, H.; DiSalvo, F. J. *J. Alloys Comp.* **1996**, *241*, 69.
 12. Park, D. G.; Gál, Z. A.; DiSalvo, F. J. *Bull. Korean Chem. Soc.* **2005**, *26*, 5.
 13. Park, D. G.; Gál, Z. A.; DiSalvo, F. J. *Bull. Korean Chem. Soc.* **2005**, *26*, 786.
 14. Park, D. G.; Gál, Z. A.; DiSalvo, F. J. *Bull. Korean Chem. Soc.* **2005**, *26*, 1543.
 15. Park, D. G.; Gál, Z. A.; DiSalvo, F. J. *J. Solid State Chem.* **2003**, *172*, 166.
 16. Park, D. G.; Gál, Z. A.; DiSalvo, F. J. *J. Alloys Comp.* **2003**, *360*, 85.
 17. Park, D. G.; Gál, Z. A.; DiSalvo, F. J. *Inorg. Chem.* **2003**, *42*, 1779.
 18. Park, D. G.; Gál, Z. A.; DiSalvo, F. J. *J. Alloys Comp.* **2003**, *353*, 107.
 19. Betz, A.; Schäfer, H.; Weiss, A. *Z. Naturforsch.* **1967**, *22b*, 103.
 20. Ewald, P. P. *Ann. Phys.* **1921**, *64*, 253.
 21. Donohue, J. *The Structures of the Elements*; Wiley: London, 1972; Chapter 6, p 236.
 22. Park, D. G.; DiSalvo, F. J. *Bull. Korean Chem. Soc.* **2008**, *29*, 2413.
 23. Verdier, P. P.; L'Haridon, P.; Marchand, M. M. R. *Acta Cryst.* **1974**, *B30*, 226.
 24. Bruker, *APEX2* (version 2.10): Software for the CCD system; Bruker Analytical X-ray System: Madison, WI, 2007.
 25. Bruker, *S.AINT Plus*: Software for the CCD system; Bruker Analytical X-ray System: Madison, WI, 2003.
 26. Sheldrick, G. M. *SADABS*; Institute für Anorganische Chemie der Universität Göttingen: Göttingen, Germany, 1999.
 27. Bruker, *XPREF* (version 6.14): Software for the CCD system; Bruker Analytical X-ray System: Madison, WI, 2003.
 28. Sheldrick, G. M. *SHELXL 97*; Institute für Anorganische Chemie der Universität Göttingen: Göttingen, Germany, 1997.
 29. Gelato, L. M.; Parthé, E. *J. Appl. Cryst.* **1987**, *20*, 139.
 30. Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837.
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