Synthesis and Crystal Structure of the New Quaternary Subnitride, \( \text{Sr}_2\text{GeGaN} \).

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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, \( \text{Sr}_2\text{GeGaN} \), which is isosstructural to its Ba analogue, \( \text{Ba}_2\text{GeGaN} \). Crystallographic data on \( \text{Sr}_2\text{GeGaN} \) are provided in Table 1-3. The crystal structure of \( \text{Sr}_2\text{GeGaN} \) is given in Figure 1. The structure of intermetallic \( \text{SrGe} \)19 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 \( \text{Sr}_2\text{GeGaN} \) is closely related to that of \( \text{SrGe} \), Figure 1c and 1d. It appears as if one \([\text{Ge}]\) in intermetallic \( \text{SrGe} \) has been replaced by \([\text{GaN}]\). This observation suggests formal charge of +1 for Ga. The empirical formula, \( \text{Sr}_2\text{GeGaN} \), can be rearranged into \( \text{Sr}_2[\text{Ge}]_2[\text{GaN}]_2^- \), which conforms to the replacement of half of \([\text{Ge}]^-\) in \( \text{SrGe} \) by \([\text{GaN}]^-\). 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 \( \text{SrGe} \), \([\text{GaN}]^-\) or \([\text{Ge}]^-\) is surrounded by the monocapped trigonal prism of \( \times \text{Sr} \). The monocapped trigonal prisms of \( \times \text{Sr} \) 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 \( \text{SrGe} \) (Figure 1c). Because of the distortion, the unitcell of \( \text{Sr}_2\text{GeGaN} \) adopts monoclinic system rather than more symmetric tetragonal one observed for \( \text{SrGe} \). It is apparent that the replacement of \([\text{Ge}]\) into \([\text{GaN}]\) 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, \( \text{Ba}_2\text{GeGaN} \). It is significantly shorter than Ge-Ge bond length, of 2.634 Å in \( \text{SrGe} \),19 and is also shorter than any known Ge-Ge distances in

Table 1. Crystallographic data for \( \text{Sr}_2\text{GeGaN} \).

<table>
<thead>
<tr>
<th>Character</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>( \text{P2}1/\text{m} )</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>( a = 6.885(1) \ \text{Å} ) ( b = 4.0432(6) \ \text{Å} ) ( c = 8.680(2) \ \text{Å} ) ( \beta = 108.454(8) \ ^\circ )</td>
</tr>
<tr>
<td>Volume</td>
<td>229.21(6) Å³</td>
</tr>
<tr>
<td>Density (calcd/ mg m⁻³)</td>
<td>4.804</td>
</tr>
<tr>
<td>Absorption coefficient (mm⁻¹)</td>
<td>35.252</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>173(2)</td>
</tr>
<tr>
<td>F(000)</td>
<td>292</td>
</tr>
<tr>
<td>Crystal size (mm⁻³)</td>
<td>0.100 × 0.025 × 0.025</td>
</tr>
<tr>
<td>θ range for data collection (°)</td>
<td>2.47 to 30.51</td>
</tr>
<tr>
<td>Index ranges</td>
<td>(-8 \leq h \leq 9, -5 \leq k \leq 5, -12 \leq l \leq 12 )</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>3617</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>792 [R(int) = 0.0401]</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>792 / 0 / 32</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.106</td>
</tr>
<tr>
<td>Final R indices</td>
<td>( R_1 = 0.0206, wR_2 = 0.0451 )</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>( R_1 = 0.0263, wR_2 = 0.0458 )</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e.Å⁻³)</td>
<td>1.125 and -0.974</td>
</tr>
</tbody>
</table>

Table 2. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10⁻³) for \( \text{Sr}_2\text{GeGaN} \).

<table>
<thead>
<tr>
<th>Wyckoff</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr(1)</td>
<td>2e</td>
<td>7978(1)</td>
<td>2500</td>
<td>339(1)</td>
</tr>
<tr>
<td>Sr(2)</td>
<td>2e</td>
<td>8154(1)</td>
<td>2500</td>
<td>6218(1)</td>
</tr>
<tr>
<td>Ge</td>
<td>2e</td>
<td>3241(1)</td>
<td>2500</td>
<td>7009(1)</td>
</tr>
<tr>
<td>Ga</td>
<td>2e</td>
<td>4647(1)</td>
<td>2500</td>
<td>2481(1)</td>
</tr>
<tr>
<td>N</td>
<td>2e</td>
<td>1767(6)</td>
<td>2500</td>
<td>1705(5)</td>
</tr>
</tbody>
</table>

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

Table 3. Anisotropic displacement parameters (Å² × 10⁻³) for \( \text{Sr}_2\text{GeGaN} \).

<table>
<thead>
<tr>
<th></th>
<th>U₁₁</th>
<th>U₂₂</th>
<th>U₃₃</th>
<th>U₁₂</th>
<th>U₁₃</th>
<th>U₂₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr(1)</td>
<td>2(1)</td>
<td>5(1)</td>
<td>3(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sr(2)</td>
<td>4(1)</td>
<td>5(1)</td>
<td>3(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ge</td>
<td>3(1)</td>
<td>5(1)</td>
<td>5(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ga</td>
<td>2(1)</td>
<td>5(1)</td>
<td>5(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>N</td>
<td>4(2)</td>
<td>6(2)</td>
<td>5(2)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The anisotropic displacement factor exponent takes the form: \(-2π^2 [h^2a^2U₁₁ + ... + 2ha*bU₁₂] \).
one-dimensional $\text{Ge}^2\text{-zig-zag chains found in ternary nitrides. The Ge-Ge bond length in the } \text{Ge}^2\text{ chain is 2.451(4), 2.5445 (7), 2.500(1), and 2.5873(9)} \AA \text{ for Sr}_2\text{GeN}_2, \text{Sr}_6\text{Ge}_5\text{N}_2 \text{, Ba}_3\text{Ge}_2\text{N}_2, \text{and Ba}_6\text{Ge}_5\text{N}_2 \text{respectively. The interatomic separation in elemental Ga or elemental Ge is 2.71, or 2.74 } \AA, \text{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 $[\text{GeN}_3]^{5-}$, tetrahedral $[\text{GeN}_4]^{4-}$, dumbell-shaped $[\text{GeN}_2]^{4-}$, or ‘bow tie’ unit of $[\text{Ge}_2\text{N}_6]^{10-}$.$^{15}$ It also clarifies the connectivity among these nitridometallate units. But, in the case of subnitrides, $\text{Ba}_2\text{GeGaN}$ or $\text{Sr}_2\text{GeGaN}$, the conventional 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 envision 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 $\text{Sr}_2\text{GeN}_2$, $\text{Sr}_6\text{Ge}_5\text{N}_2$, $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$, or $\text{Sr}_2\text{GeMgN}_4$.\n
Figure 2a and 2b show the coordination spheres around elements in negative formal charges. $\text{N}^{3-}$ is coordinated to 6 cations (5 × $\text{Sr}^{2+}$ and 1 × $\text{Ga}^{1+}$) into the pseudo-octahedron of $[\text{Sr}_5\text{GaN}]$ in Figure 2a. The octahedral coordination has been most commonly observed for $\text{N}$ in other known metal nitride compounds.$^{2-1\text{8}}$ The bond lengths of $\text{Sr}-\text{N}$ [2.501(4)-2.732(3) Å] are in the range of distances observed in other nitrides, and that of $\text{Ga}-\text{N}$ [1.882(4) Å] is also similar to the ones in other nitrides. The coordination sphere around $\text{Ge}^{2-}$ is crowder than that around $\text{N}^{3-}$, alluding to the difference of ionic sizes between them. $\text{Ge}^{2-}$ is coordinated to 9 cations (7 × $\text{Sr}^{2+}$ and 2 × $\text{Ga}^{1+}$) into distorted tri-capped trigonal prism of $[\text{Sr}_7\text{Ga}_2\text{Ge}]$ (Figure 2b). As seen in Figure 1d, $\text{Ge}^{2-}$ is coordinated to 7 ×

**(Figure 1.** Comparison between crystal structures of $\text{Sr}_2\text{GeGaN}$ and $\text{SrGe}$. (a) The structure of $\text{Sr}_2\text{GeGaN}$ viewed along b-axis, and (b) along c-axis. (c) The structure of $\text{SrGe}$ viewed along c-axis, and (d) along a-axis. Symmetric tetragonal unit-cell of $\text{SrGe}$ is distorted into monoclinic one of $\text{Sr}_2\text{GeGaN}$, as $[\text{Ge}]^{2-}$ is replaced by $[\text{GaN}]^{2-}$.

**(Table 4.** Bond valences and Madelung potentials from Eutax for $\text{Sr}_2\text{GeGaN}$.

<table>
<thead>
<tr>
<th>Bond valences</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sr}(1)$ = 1.61</td>
<td></td>
</tr>
<tr>
<td>$\text{Sr}(2)$ = 1.45</td>
<td></td>
</tr>
<tr>
<td>$\text{Ga}$ = 2.39</td>
<td></td>
</tr>
<tr>
<td>$\text{Ge}$ = 2.99</td>
<td></td>
</tr>
<tr>
<td>$\text{N}$ = 2.46</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Madelung site potentials</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
<td>Pot(V)</td>
</tr>
<tr>
<td>------</td>
<td>--------</td>
</tr>
<tr>
<td>$\text{Sr}(1)$</td>
<td>-18.84</td>
</tr>
<tr>
<td>$\text{Sr}(2)$</td>
<td>-16.11</td>
</tr>
<tr>
<td>$\text{Ga}$</td>
<td>-14.12</td>
</tr>
<tr>
<td>$\text{Ge}$</td>
<td>16.67</td>
</tr>
<tr>
<td>$\text{N}$</td>
<td>26.32</td>
</tr>
</tbody>
</table>

**(Figure 2.** Coordinations around elements in negative formal charges. (a) $\text{N}^{3-}$ coordinates to $6 \times$ cations into octahedron of $[\text{Sr}_5\text{GaN}]$. (b) $\text{Ge}^{2-}$ coordinates to $9 \times$ cations into distorted tri-capped trigonal prism of $[\text{Sr}_7\text{Ga}_2\text{Ge}]$.\n
Notes
The diffraction data was carried out by the program SAINT. The atomic parameters were standardized using SHELXL. The space group was verified by using ADDSYM. Bond valence and Madelung potential was calculated by EUTAX. 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 Ga3Sr (silvery) and Sr2GeGaN (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), β = 108.454(8)°, c = 8.680 (2) 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 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 (± 0.01), 2.0 (± 0.1), and 0.97 (± 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 P21/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 Sr2GeGaN.

Supplementary Material. Supplementary material has been sent to Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (crystaldata@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


Notes

Sr2+ into mono-capped trigonal prism of [Sr7Ge2] in SrGe. It is interesting to note that Ge2- accommodates two more cations (2 × Ga2+) into its coordination sphere, when alternating [Ge2-] of SrGe is replaced by [GaN]2-, turning it into Sr2GeGaN. The bond lengths of Sr-Ge range from 3.3392(7) to 3.6586(8) Å. These tri-capped trigonal prisms of [Sr2Ga2Ge] and octahedrons of [Sr2GaGe] share their faces and edges into the space filling version of the crystal structure of Sr2GeGaN, shown in Figure 3. One might conceive getting a new material such as Sr2GeGaN or BaGaN by replacing the remaining Ge2- into [GaN]2-. Such a material, Sr2GeGaN 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 Sr2GeGaN cannot be replaced by another set of [GaN] without disrupting the current structural theme originated from SrGe. Only an analogue known to date is CaGaN, and as can be anticipated, its layered structure doesn’t share any structural theme which can be traced back to Sr2GeGaN or SrGe.

Experimental

Sr2GeGaN was synthesized as single crystals from constituent elements in molten Na by the Na-flux method, as described in previous reports on other nitrides. Reactants used for the synthesis were NaN3 (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. The integration of the diffraction data was carried out by the program SAINT. An empirical absorption correction was applied using SADABS. The initial input file for solving the crystal structure was prepared by XPREP. The structure was solved by the direct method, using SHELXS. Refinement of the structure was carried out by the full-matrix least square method (on F2), using SHELXL. The atomic parameters were standardized using SHELXD. The space group was verified by using ADDSYM. Bond valence and Madelung potential was calculated by EUTAX. 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.

Figure 3. Polyhedral representation of the crystal structure of Sr2GeGaN, constructed from the anion-centered polyhedral perspective. Polyhedral subunit in dark shade is tri-capped trigonal prism of [Sr7Ga2Ge], and one in light shade is octahedron of [Sr2GeGaN], shown in Figure 2.