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Synthesis and Structure of Sr_3GaN_3 and Sr_6GaN_5: Strontium Gallium Nitrides with Isolated Planar $[GaN_3]^{6-}$ Anions

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Two new strontium gallium nitrides were obtained as single crystals by reaction in molten Na. Black Sr_3GaN_3 is isostructural with its transition metal analogues, Sr_3MnN_3, Ba_3MnN_3, Sr_3CrN_3, Ba_3CrN_3, and Ba_3FeN_3, and is the first example of a 313-ternary nitride containing only main group metals. It crystallizes in space group $P6_3/m$ (No. 176) with $a = 7.584(2)$ Å, $c = 5.410(3)$ Å, and $Z = 2$. Black Sr_6GaN_5 is isostructural with Ca_6GaN_5 and also with its transition metal analogues, Ca_6MnN_5 and Ca_6FeN_5. It crystallizes in space group $P6_3/mcm$ (No. 193) with $a = 6.6667(6)$ Å, $c = 12.9999(17)$ Å, and $Z = 2$. Both Ga compounds contain isolated planar $[GaN_3]^{6-}$ nitridometallate anions of D_{3h} symmetry.

Introduction

Many new ternary and quaternary nitrides with diverse structures have been recently reported.[1−8] Particularly, the use of Na melts provides a very productive route to obtain single crystals of many ternary nitrides with interesting structures and properties.[9−19] In most cases, an alkaline earth metal is introduced into a Na melt to enhance the solubility of nitrogen, and is incorporated in the nitride product. The structures of those nitrides have been described as isolated or condensed nitridometallate anions and alkaline earth metal cations. Many ternary metal nitrides, which contain alkaline earth metals and main group metals, exhibit structural features that are quite different from those in metal oxides. For example, tetrahedral nitridometalates of Ga, Si, and Ge often share their edges, whereas only corners are shared in the corresponding oxides.[12,13,15−18] Only two strontium gallium nitrides, $Sr_3Ga_3N_5$ and $Sr_3Ga_2N_4$, have been previously reported.[15] They contain GaN_4 tetrahedra connected through their edges and corners. The GaN_4 tetrahedra are condensed into a three-dimensional framework in $Sr_3Ga_3N_5$ or one-dimensional chains in $Sr_3Ga_2N_4$. The dimensionality of the nitridogallate anion network decreases as the stoichiometry becomes more alkaline earth rich. Our effort to obtain higher degrees of condensation of nitridogallate tetrahedra by lowering the Sr content has not yet been successful. Instead, by exploiting the Sr-rich region of the phase diagram, we obtained two more strontium gallium nitrides, Sr_3GaN_3 and Sr_6GaN_5, which contain isolated GaN_3 planar anions, rather than GaN_4 tetrahedra.

Experimental Section

The strontium gallium nitrides were synthesized in containers made out of Nb tubing (110 mm length, 9.5 mm o.d., and 1 mm thickness), with one end closed by welding in an Ar atmosphere, using a Centorr Associates arc furnace. Before welding, the tubing was cleaned in a concentrated mixture of hydrofluoric, nitric, and sulfuric acids (15:40:45 by volume). ***CAUTION:*** *This is an extremely corrosive mixture. Contact with skin is hazardous and may be fatal.* Under argon in a VAC drybox, a niobium container was loaded with NaN_3 (91.2 mg, Aldrich, 99%), Na (199.6

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(1) Niewa, R.; DiSalvo, F. J. *Chem. Mater.* **1998**, *10*, 2733.
(2) Schnick, W.; Huppertz, H. *Chem. Eur. J.* **1997**, *3*, 679.
(3) Simon, A. *Coord. Chem. Rev.* **1997**, *163*, 253.
(4) Kniep, R. *Pure Appl. Chem.* **1997**, *69*, 185.
(5) DiSalvo, F. J.; Clarke, S. J. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 241.
(6) Niewa, R.; Jacobs, H. *Chem. Rev.* **1996**, *96*, 2053.
(7) Röhr, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1199.
(8) Schleid, T. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 227.
(9) Yamane H.; Sasaki, S.; Kuboda, S.; Inoue, R.; Shimada, M.; Kajiwara, T. *J. Solid State Chem.* **2002**, *163*, 449.
(10) Kowach, G. R.; Brese, N. E.; Bolle, U. M.; Warren, C. J.; DiSalvo, F. J. *J. Solid State Chem.* **2000**, *154*, 542.
(11) Yamane, H.; DiSalvo, F. J. *J. Solid State Chem.* **1995**, *119*, 375.
(12) Clarke, S. J.; DiSalvo, F. J. *Inorg. Chem.* **2000**, *39*, 2631.
(13) Clarke, S. J.; DiSalvo, F. J. *J. Alloys Compd.* **1998**, *274*, 118.
(14) Clarke, S. J.; DiSalvo, F. J. *J. Alloys Compd.* **1997**, *259*, 158.
(15) Clarke, S. J.; DiSalvo, F. J. *Inorg. Chem.* **1997**, *36*, 1143.
(16) Clarke, S. J.; Kowach, G. R.; DiSalvo, F. J. *Inorg. Chem.* **1996**, *35*, 7009.
(17) Yamane, H.; DiSalvo, F. J. *Acta Crystallogr.* **1996**, *C52*, 760.
(18) Yamane, H.; DiSalvo, F. J. *J. Alloys Compd.* **1996**, *240*, 33.
(19) Yamane, H.; DiSalvo, F. J. *J. Alloys Compd.* **1996**, *241*, 69.

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mg, Aldrich, 99%), Ga (38.4 mg, Cerac, 99.999%), Sr (192.4 mg, Aldrich, 99+%), and Li (3.8 mg, Aldrich, 99.9%). We were hoping to prepare quaternary phases containing both Li and Sr, but under the present conditions no Li is included in the crystals studied. The molar ratio of Na:Ga:Sr:Li was 18:1:4:1. The container was sealed by welding its open end in an argon atmosphere with active water-cooling so that NaN_3 did not decompose due to heating during the welding. In order to protect the container from oxidation during heat treatment, the sealed niobium container was put into quartz tubing, which was then sealed under vacuum. The reaction container was then heated in a muffle furnace. The temperature was raised to 760 °C over 15 h, maintained at that temperature for 48 h, and lowered linearly to 200 °C over 200 h. Thereafter, the furnace was turned off. Na was separated from the product by sublimation at 300 °C under dynamic vacuum.

Single crystals of strontium gallium nitride were mounted on a layer of poly(butene) oil sustained in a plastic loop by its surface tension. By placing it in a cold nitrogen gas flow, the oil was immediately solidified. The crystal was protected from contact with air by the oil and the flow of nitrogen gas. A Bruker SMART system with a CCD detector collected X-ray diffraction data (Mo Kα wavelength 0.71073 Å). Integration of the diffraction data was carried out by using the SAINT software.[20] An empirical absorption correction was applied using SADABS.[21] A face-indexed analytical absorption correction was also applied to the collected diffraction intensity data with the program XPREP.[22] The structure was solved by the Direct method, using SHELXS.[23] Refinement of the structure was carried out by the full-matrix least-squares 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] Bond valence calculations and Madelung potentials were obtained by the program EUTAX.[26]

Table 1. Crystallographic Data for Sr_3GaN_3 and Sr_6GaN_5

	Sr_3GaN_3	Sr_6GaN_5
a/Å	7.584(2)	6.6667(6)
b/Å	7.584(2)	6.6667(6)
c/Å	5.410(3)	12.9999(17)
γ/deg	120	120
V/Å^3	269.51(17)	500.37(9)
Z	2	2
space group	$P6_3/m$ (No. 176)	$P6_3/mcm$ (No. 193)
fw	374.6	665.49
D(calcd)/g cm^{-3}	4.616	4.417
T/K	235(2)	173(2)
GOF on F^2	1.274	1.271
final R indices $[I > 2\sigma(I)]^a$	R1 = 0.0326, wR2 = 0.0807	R1 = 0.0421, wR2 = 0.0868
R indices (all data)^a	R1 = 0.0363, wR2 = 0.0818	R1 = 0.0460, wR2 = 0.0876

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^2)^2]^{1/2}$, where $w = 1/\sigma(F_o^2)^2 + (gP)^2 + jP]$, $P = [\max(F_o^2,0) + 2F_c^2]/3$. $g = 0.0287$, $j = 2.2654$ for Sr_3GaN_3, and $g = 0.0348$, $j = 4.8694$ for Sr_6GaN_5.

Table 2. Atomic Parameters for Sr_3GaN_3

atom	site	x	y	z	U_{eq}^a
Sr	6h	0.3568(1)	0.2838(1)	0.2500	7(1)
Ga	2c	0.3333	0.6667	0.2500	6(1)
N	6h	0.922(11)	0.3988(11)	0.2500	9(1)

[a] The equivalent isotropic thermal displacement parameter, U_{eq} in Å^3 × 10^3, is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Anisotropic Displacement Parameters (Å^3 × 10^3) for Sr_3GaN_3^{a}

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr	8(1)	8(1)	7(1)	0	0	5(1)
Ga	6(1)	6(1)	6(1)	0	0	3(1)
N	7(3)	6(3)	12(3)	0	0	3(3)

[a] The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table 4. Atomic Parameters for Sr_6GaN_5

atom	site	x	y	z	U_{eq}^a
Sr	12k	0.5953(1)	0	0.1237(1)	7(1)
Ga	2a	0	0	0.2500	3(1)
N2	4d	0.3333	0.6667	0	9(2)
N1	6g	0.2843(15)	0	0.2500	10(2)

[a] The equivalent isotropic thermal displacement parameter, U_{eq} in Å^3 × 10^3, is defined as one-third of the trace of the of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Anisotropic Displacement Parameters (Å^3 × 10^3) for Sr_6GaN_5^{a}

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr	7(1)	6(1)	6(1)	0	-2(1)	3(1)
Ga	3(1)	3(1)	4(1)	0	0	1(1)
N(2)	9(3)	9(3)	9(6)	0	0	5(2)
N(1)	6(3)	6(4)	18(5)	0	0	3(2)

[a] The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Results and Discussion

The product was obtained as a black powder. Under the microscope, three different types of single crystals were observed. Single crystals of Sr_3GaN_3 were black multifaceted prisms with reflecting surfaces. Single crystals of Sr_6GaN_5 were thick black plates with multifaceted edges. The product also contained very thin black plates with a layered texture along the edges. The structure determination of these thin plates has not yet been successful. All crystals were reactive toward moisture, but could be handled in poly(butene) oil for several days without degradation. Semiquantitative (without standards) EDX (energy-dispersive X-ray) analysis on several crystals of each different shape showed that the Sr:Ga molar ratio was close to the ideal ratio of 3:1 or 6:1 within error (±2.5%). No other elements or Na were detected by the analysis. Nitrogen in the crystal was qualitatively identified by WDX (wavelength dispersive X-ray) analysis. Although Li was included in the reaction mixture, it is not included in the crystals we examined, at least as far as we can ascertain by diffraction and by stoichiometries that satisfy the octet rule. Crystallographic information for Sr_3GaN_3 and Sr_6GaN_5 are provided in Tables 1 through 7.

Structure of Sr_3GaN_3. Sr_3GaN_3 is isostructural with Sr_3MnN_3, Ba_3MnN_3, Sr_3CrN_3, Ba_3CrN_3, and Ba_3FeN_3 (313 stoichiometry), which contains isolated trigonal planar $[MN_3]$ units (M = Mn, Cr, or Fe) of D_{3h} symmetry.[27–29] The

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(20) *SAINT Plus: Software for the CCD system*; Bruker Analytical X-ray System: Madison, WI, 1999.

(21) Sheldrick, G. M. *SADABS*; Institut für Anorganische Chemie der Universität Göttingen: Göttingen, Germany, 1999.

(22) *XPREP*; Bruker Analytical X-ray System: Madison, WI, 1999.

(23) Sheldrick, G. M. *SHELXL 97*; Institut für Anorganische Chemie der Universität Göttingen: Göttingen, Germany, 1997.

(24) Gelato, L. M.; Parthé, E. *J. Appl. Crystallogr.* **1987**, *20*, 139.

(25) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(26) Ewald, P. P. *Ann. Phys.* **1921**, *64*, 253.

Table 6. Selected Atomic Separations (Å) and Bond Angles (deg) in Sr_3GaN_3

	Ga-Centered Triangle		
Ga^a-N^a	1.938(7)	$N^a-Ga^a-N^a$	120.000(1)
	N-Centered Pseudo-octahedron		
Sr^a-N^a	2.557(7)	$Ga^a-N^a-Sr^a$	78.4(2)
Sr^a-N^a	2.682(8)	$Ga^a-N^a-Sr^a$	82.4(3)
Sr^a-N^a	2.707(8)	$Sr^a-N^a-Sr^a$	89.3(2)
Sr^b-N^a	2.7193(15)	$Sr^a-N^a-Sr^a$	109.9(3)
		$Ga^a-N^a-Sr^b$	95.17(16)
		$Sr^a-N^a-Sr^b$	85.53(16)
		$Sr^a-N^a-Sr^b$	88.01(16)
		$Sr^a-N^a-Sr^b$	93.68(16)
		$Sr^b-N^a-Sr^b$	168.3(3)

^{a} In same *ab*-plane. ^{b} Out of the plane.

Table 7. Selected Atomic Separations (Å) and Bond Angles (degree) in Sr_6GaN_5

	Ga-Centered Triangle		
Ga−N1	1.895(10)	N1−Ga−N1	120.000(1)
	Sr-Centered Pseudo Square Pyramid		
Sr^a-N2^a	2.5874(5)	$N2^a-Sr^a-N2^a$	96.11(2)
Sr^a-N1^a	2.907(2)	$N1^a-Sr^a-N1^a$	68.7(4)
Sr^a-N1^b	2.644(8)	$N2^a-Sr^a-N1^a$	94.52(16)
		$N2^a-Sr^a-N1^a$	156.73(19)
		$N1^a-Sr^a-N1^b$	97.0(2)
		$N2^a-Sr^a-N1^b$	101.16(9)
	N2-Centered Pseudo-octahedron		
Sr−N2	2.5874(5)	$Sr^c-N2-Sr^d$	83.89(2)
		$Sr^c-N2-Sr^c$	85.42(2)
	N1-Centered Pseudo Monocapped Trigonal Prism		
Sr−N1	2.644(8)	$Sr^e-N1-Sr^e$	106.98(11)
Sr−N1	2.907(2)	$Sr^e-N1-Sr^e$	78.28(9)
Ga−N1	1.895(10)	$Sr^e-N1-Sr^f$	68.74(6)
		$Sr^f-N1-Sr^f$	76.7(3)

^{a} In the puckered pseudo square base. ^{b} In the apex of the pseudo square pyramid. ^{c,d,e,f} In the same *ab*-plane, respectively.

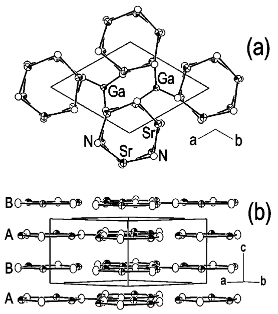

Figure 1. Structure of Sr_3GaN_3, (a) seen along [001] (b) and seen along [110]. The thermal ellipsoids are shown at 99% level. N atoms are shown as spheres. For simplification, only Sr−N bonds in the range 2.557−2.682 Å are shown. Thereby, the layered feature [...ABAB...] of the structure is exaggerated. Planar six-membered rings of alternating Sr and N generate open channels along the *c*-axis. GaN_3 units join the channels together.

nitridogallate ($[GaN_3]^{6-}$) anions are isolated from each other by the Sr countercations. Even though the triangular $[MN_3]$ is commonly found as an isolated unit in many different ternary transition metal nitrides (M = V, Cr, Mn, Fe, Co),[27−33] in main group element metal nitrides, it has been observed only in Ca_6GaN_5.[34] There is an early report on the synthesis of Mg_3GaN_3,[35] but it contains an unindexed powder pattern and fails to establish any structural details of the compound, though the elemental analysis confirms the reported 313 stoichiometry.

Identical Ga−N bond lengths are 1.938 Å. In condensed GaN_4 anions, the Ga−N bond lengthens as the N is shared by more adjacent Ga.[15−17] Without having any Ga−N−Ga interactions, the Ga−N bond in GaN_3 is expected to be quite short. Indeed, reported Ga−N bond lengths in other Ga nitrides range from 1.926 to 2.068 Å.[13,15,17,34−38] The range of bond lengths is 1.965−2.057, 1.950−2.047, or 1.937−2.002, for edge-sharing bridging bonds, corner-sharing bonds, or terminal ones, respectively. When the structure is viewed along the *c*-axis, as in Figure 1a, channels along the axis are apparent. The channel is surrounded by planar six-membered rings of alternating Sr and N, stacked on each other in a staggered fashion. The isolated $[GaN_3]$ units are ordered on (001) planes. Since all the Sr are also located on these planes, the overall structure can be described as an [...ABABAB...] stacking of layers along the *c*-axis. The out-of-plane Sr−N bond (2.719 Å) is longer than bonds around the channel, which range from 2.557 to 2.682 Å. In Figure 1b, the structure of Sr_3GaN_3 is shown as a stacking of those layers. Only the in-plane Sr−N bonds are shown; thereby the layered nature of the structure is exaggerated.

The structure of a crystal is interpreted in a specific way, often to emphasize certain aspects of the structure, as was done in Figure 1. An informative way to construct a simplified perspective of the crystal structure is to introduce polyhedral units. Unlike the case of oxide compounds, whose structure is represented commonly by cation-centered polyhedral units, we find that it is often instructive to also construct N-centered polyhedral units. Some oxide compounds, such as Cs_3O or $Rb_nCs_{11}O_3$ ($n = 1$, 2, or 7), are best described by anion-centered polyhedra.[39,40] In most ternary metal nitrides, nitrogen is six-coordinate to surrounding metals. Likewise, in Sr_3GaN_3, nitrogen is coordinated to six metals, one Ga and five Sr, generating a heavily distorted octahedron. The overall structure of Sr_3GaN_3 can also be described as a systematic stacking of this basic pseudo-octahedral unit. In Figure 2a, the distorted octahedron around nitrogen, $[Sr_5GaN]$, is shown. By sharing apical Ga, three distorted octahedra combine into a basic building block, which appears as a triangular shape looking parallel to [001], as shown in Figure 2b. This building block, $[Sr_{12}GaN_3]$,

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(27) Tennstedt, A.; Röhr, C.; Kniep, R. *Z. Naturforsch.* **1993**, *48b*, 794.
(28) Barker, M. G.; Begley, M. J.; Edwards, P. P.; Gregory, D. H.; Smith, S. E. *J. Chem. Soc., Dalton Trans.* **1996**, 1.
(29) Höhn, P.; Kniep, R.; Rabenau, A. *Z. Kristallogr.* **1991**, *196*, 153.
(30) Vennos, D. A.; DiSalvo, F. J. *J. Solid State Chem.* **1992**, *98*, 318.
(31) Vennos, D. A.; Badding, M. E.; DiSalvo, F. J. *Inorg. Chem.* **1990**, *29*, 4059.
(32) Tennstedt, A.; Röhr, C.; Kniep, R. *Z. Naturforsch.* **1993**, *48b*, 1831.
(33) Yamamoto, T.; Kikkawa, S.; Kanamaru, F. *J. Solid State Chem.* **1995**, *119*, 161.
(34) Cordier, G.; Höhn, P.; Kniep, R.; Rabenau, A. *Z. Anorg. Allg. Chem.* **1990**, *591*, 58.
(35) Verdier, P.; Marchand, R.; Lang, J. *C. R. Seances Acad. Sci.* **1970**, *271*, 1002.
(36) Cordier G. *Z. Naturforsch.* **1988**, *43B*, 1253.
(37) Juza, R.; Hahn, H. *Z. Anorg. Allg. Chem.* **1938**, *239*, 282.
(38) Juza, R.; Hahn, H. *Z. Anorg. Allg. Chem.* **1948**, *257*, 13.
(39) Tsai, K.-R.; Harris, P. M.; Lassettre, E. N. *J. Phys. Chem.* **1956**, *60*, 345.
(40) Deiseroth, H.-J.; Simon, A. *Rev. Chim. Miner.* **1983**, *20*, 475.

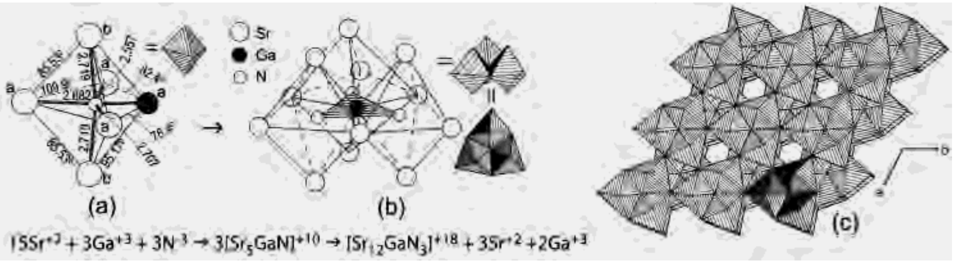

Figure 2. (a) Coordination around N, which generates the pseudo-octahedron of $[Sr_5GaN]$. Atoms in the *ab*-plane are labeled as a, and atoms out of the plane are labeled as b (refer to Table 6). (b) Hypothetical building block of $[Sr_{12}GaN_3]$ is defined by merging three of those pseudo-octahedra in such a manner that Ga is in the center of the block (edge-sharing). (c) Polyhedral representation of Sr_3GaN_3 is obtained by stacking those building blocks in a regular manner.

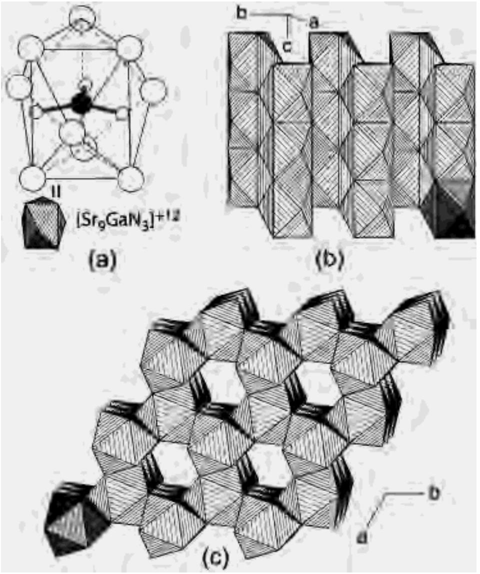

Figure 3. (a) Coordination around Ga, which generates a tricapped trigonal prism of $[Sr_9GaN_3]$. By sharing faces on top and bottom, these repeating blocks stack up into columns. By sharing edges with adjacent ones, the columns generate a polyhedral representation of Sr_3GaN_3, (b) which is seen along the *a*-axis (c) and along the *c*-axis.

contains GaN_3^{6-} in the middle, which is then surrounded by twelve Sr^{2+}. Layers built from $[Sr_{12}GaN_3]$ are alternately stacked along the *c*-axis in ...ABAB... fashion, resulting in extensive edge-sharing. Each Sr is shared by four different building blocks, two in the layer, one from the layer above, and one from the layer below. The empirical formula of the compound can thus be written as $Sr_{12/4}GaN_3$. Stacked up in a repeating manner, they build up to the polyhedral representation of the structure, shown in Figure 2c. During the process of stacking, each octahedron shares eight of its 12 edges and all six corners with adjacent octahedra.

The building block of three condensed octahedra introduced above has Ga at the center. By removing the three Sr furthest from the Ga, a different polyhedral representation of the structure is obtained. In Figure 3a, the resulting local structure around Ga is shown to include three N and nine Sr. The cations generate a tricapped trigonal prism, which encloses the nitridogallate anion in the middle. Using this prism, a different polyhedral representation of the structure is generated (Figure 3b,c). Because each Sr is shared by three adjacent building blocks, the empirical formula of the building block becomes $Sr_{9/3}GaN_3$. By sharing the top and bottom triangular faces of the prism, the building blocks stack up in columns along the *c*-axis. These columns connect side by side by sharing half of their side edges, generating the structure of Sr_3GaN_3 in Figure 3b.

In all the schemes presented to look at the structure, Figures 1, 2, and 3, channels are apparent along the *c*-axis. The distance between opposing Sr and N within the channel is 5.218 Å. These channels undulate in diameter. The smallest diameter (at $z = 0.25$) can be estimated by using either ionic or van der Waals radii for the six surrounding Sr and N. Using $r_{\text{ionic}}(Sr^{2+}) = 1.32$ Å and $r_{\text{ionic}}(N^{3-}) = 1.71$ Å, we obtain an internal diameter of 2.19 Å. Using $r_{\text{vdw}}(Sr^{2+}) = 2.15$ Å and $r_{\text{vdw}}(N^{3-}) = 1.55$ Å, we obtain 1.518 Å. The largest diameter is at $z = 0$, which is between two layers of atoms (see Figure 1). The distance between opposing Sr and Sr in two adjacent layers within the channel is 5.643 Å. Using the same radii, the internal diameter of this hole is 3.00 Å (ionic) or 1.34 Å (van der Waals). We expect the “true” diameter to be somewhere between these extremes. The Madelung potential calculated in the center of the channel is practically zero, -0.582 V at (0, 0, $^1/_4$), and -0.683 V at (0, 0, 0). Even though the size of the channel is big enough for small ions, such as Li^+, the potential at the center of the channel suggests no preference for the insertion of ions.

Structure of Sr_6GaN_5. Sr_6GaN_5 is isostructural with Ca_6MnN_5, Ca_6FeN_5, and Ca_6GaN_5.[34,41] Nitridogallate anions, $[GaN_3]^{6-}$, again of D_{3h} symmetry, are arranged on (001) planes, thereby generating a layer containing only nitridogallate anions. The layers are rotated by 60° and stacked along the *c*-axis. The nitridogallate layers are separated by layers composed of edge-sharing octahedral units of $[Sr_6N]$. Thereby, Sr_6GaN_5 also has layered structure, as shown in Figure 4. The Ga−Ga distance along the *c*-axis is slightly shorter (6.495 Å) than the in-plane distance (6.667 Å).

Again the structure may be described as polyhedral packings in several different ways. We start by considering metallate anions: GaN_3 and SrN_5. Each Sr is bound to five N (2 × N2 and 3 × N1) in a distorted square pyramidal unit of $[Sr_5N]$ shown in Figure 5a. Six of these square pyramids are connected via their corners in a superoctahedron to generate a closed inner space, shown in Figure 5b,c. The top and bottom faces of the superoctahedron are centered

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(41) Gregory, D. H.; Barker, M. G.; Edwards, P. P.; Siddons, D. J. *Inorg. Chem.* **1995**, *34*, 5195.

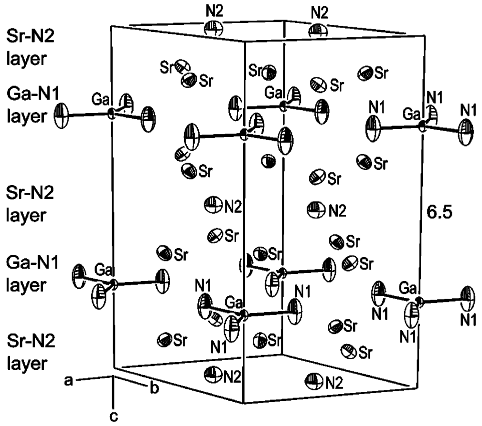

Figure 4. Structure of Sr_6GaN_5. The thermal ellipsoids are shown at the 99% level. For simplification, only Ga−N bonds are shown.

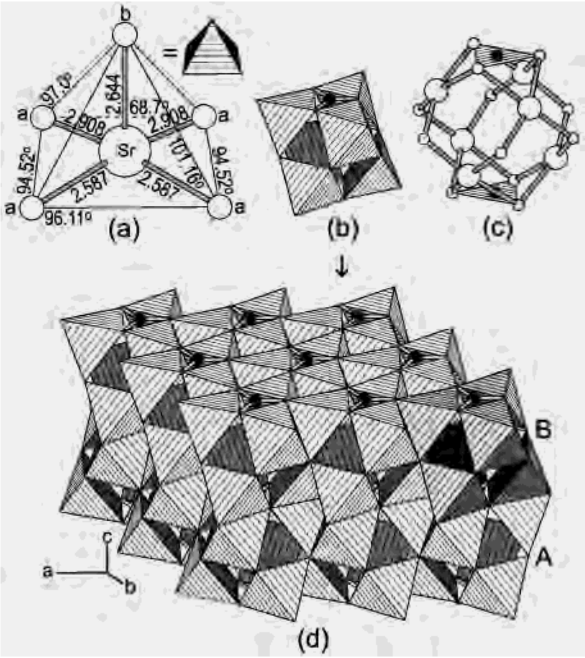

Figure 5. (a) Coordination around Sr, which generates a pseudo square pyramid. The atoms in the puckered square base are labeled as a (refer to Table 7). (b) Six of those pseudo square pyramids combine with two $[GaN_3]$, defining a repeating block of superoctahedron. (c) An empty space in the center is viewed better by removing vertices (six N) of the superoctahedron. (d) By stacking up the blocks in a regular manner, the polyhedral representation of Sr_6GaN_5 is obtained.

by GaN_3 units. In between those two nitridogallates, a cavity of substantial size is present, as defined by the two nitridogallates and six square pyramidal units of $[Sr_5N]$. The nucleus-to-nucleus distance between opposing Sr within the cavity is 6.277 Å, and that between N is 7.529 Å. Again using hard sphere ionic radii, or van der Waals radii, the cavity diameter is calculated to be between 3.637 Å (ionic) and 1.977 Å (van der Waals). Assuming ionic charges equal to oxidation states, the Madelung potential calculated at the center of the cavity, (0, 0, $^1/_2$), has a slightly positive value (+3.528 V).

Another way to look at the structure is to consider N-centered building blocks, which can be assembled into the product. Around N in two crystallographically inequivalent sites (N1 and N2), two different types of polyhedral units are obtained. In most metal nitrides, N coordination is six. As seen in Figure 6a, N2 bonds to six Sr to generate nearly octahedral $[Sr_6N]$. Two of these octahedra are connected by edge-sharing to form $[Sr_{10}N_2]$, which serves as a building block to generate a slab of $[Sr_9N_4]_n^{6n+}$ (shown in Figure 8a) by sharing two of their side edges. Unlike N2, N1 is coordinated to seven metal atoms, six Sr and one Ga, to generate a monocapped triangular prism of $[Sr_6GaN]$, as shown in Figure 7a. Three of these units connect by sharing an apical Ga to form a unit of $[Sr_{12}GaN_3]$ in roughly triangular shape with a concave center (Figure 7b). This building block contains the triangular nitridogallate anion in the middle, surrounded by 12 Sr cations. By sharing their

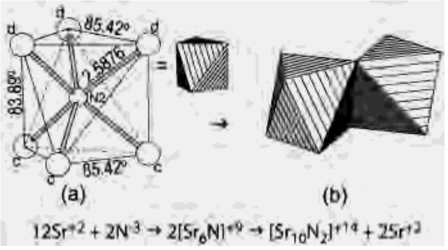

Figure 6. (a) Coordination around N2, which generates a distorted octahedron of $[Sr_6N]$. (b) By sharing an edge, two of those $[Sr_6N]$ generate a building block of $[Sr_{10}N_2]$.

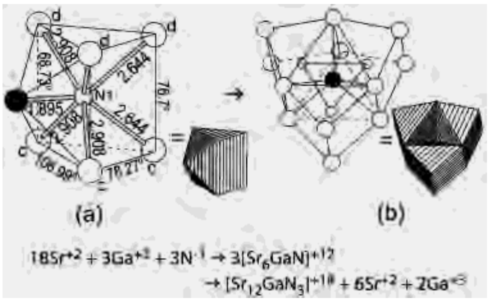

Figure 7. (a) The coordination geometry around N1 generates a monocapped trigonal prism of $[Sr_6GaN]$. (b) A hypothetical building block of $[Sr_{12}GaN_3]$ is defined by merging three of those monocapped trigonal prisms in such a manner that Ga is in the center of the block (face-sharing). Compare to the edge-sharing of $[Sr_5GaN]$ in Figure 3.

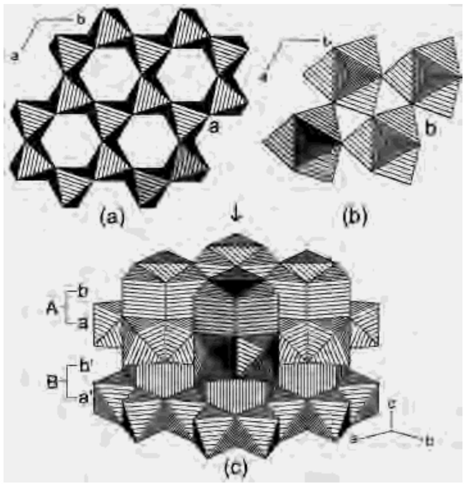

Figure 8. (a) Two-dimensional slab of $[Sr_9N_4]_n^{6n+}$, which is generated by edge-sharing of $[Sr_{10}N_2]$ (in Figure 7). (b) Two-dimensional slab of $[GaSr_6N_3]_n^{6n+}$, which is generated by edge-sharing of $[Sr_{12}GaN_3]$ (in Figure 8). (c) By stacking up those two slabs in a regular manner, a polyhedral representation of Sr_6GaN_5 is obtained.

side edges, these building blocks generate a two-dimensional slab of $[GaSr_6N_3]_n^{6n+}$, whose structure was shown in Figure 8b. Therefore, each type of building block leads to a two-dimensional slab of its own characteristic conformation. By stacking one kind of slab over the other kind in an alternating way of [...ABAB...], a polyhedral representation of the Sr_6GaN_5 can be obtained as in Figure 8c.

Note that the Ga−N bond length in Sr_6GaN_5 (1.895 Å) is shorter than that in Sr_3GaN_3 (1.938 Å). The former is 0.04 Å shorter than the shortest end of the general range of Ga−N bond lengths observed in known Sr−Ga nitrides. These two compounds provide a rare example for a valid comparison of the influence of the surrounding environment on specific bond characteristics. In both cases, the triangular unit of $[GaN_3]$ is well isolated from others, and is surrounded solely by Sr. The Ga−N local structures are shown in Figures 2a and 7a. In the monocapped triangular prismatic $[Sr_6GaN]$, N is coordinated by six Sr, and Sr−N bond lengths range from 2.644 to 2.908 Å. In the octahedral $[Sr_5GaN]$, N is coordinated by five Sr, and the Sr−N bond lengths range from 2.557 to 2.719 Å. Apparently, by adding one more Sr around N, the Ga−N bond is shortened significantly. At the same time, the average Sr−N bond length increased. Therefore, the addition of one more Sr into the coordination sphere apparently drew electron density out of the Sr−N bonds and dumped it into the Ga−N bond. It is also interesting to note that the Ga−N bond length in the isostructural Ca_6GaN_5 (1.951 Å) is a little longer than the one in Sr_6GaN_5 (1.938 Å).[34] Since Sr is more electropositive than Ca, it is more electron-donating. These observations are consistent with the expectations of the inductive effect on the bond length.[42] Calculations by the bond valence method[43,44] give under-valued valences for the constituents: Sr = 1.418, Ga = 2.597, N1 = 2.167 and Sr = 1.517, Ga = 2.301, N = 2.284, for Sr_6GaN_5 and Sr_3GaN_3, respectively. These bond valence sums are empirical values generated from tables of average single bond lengths and, thus, show some deviation from the expected values of 2 and 3 for Sr and Ga, respectively. However, by comparing these two sets of valences, the trend implied by the inductive effect can be easily seen. The valence for Sr is smaller, and that for Ga is larger in Sr_6GaN_5 than in Sr_3GaN_3.

The understanding of the extended structure obtained by condensing small N-centered polyhedral units is well demonstrated in the crystal structures of subnitrides. The structure of $Na_{16}Ba_6N$ (and $Ag_{16}Ca_6N$) contains isolated octahedral $[AE_6N]$ (AE = Ca or Ba).[45] Edge-sharing of the octahedral $[Ba_6N]$ generates a one-dimensional extended structure of $NaBa_3N$,[46] or of Na_5Ba_3N.[47] Corner-sharing of the octahedral $[Ca_6N]$ leads to the two-dimensional or the three-dimensional extended structure of Ca_4In_2N[48] or of Ca_3AuN,[49] respectively. Isolated $[AE_6N]$ are also contained in Sr_6Ga_5N and Ba_6Ga_5N.[50] It was also shown that the mixed alkaline earth metal $[Ba_{14}CaN_6]$ cluster which is contained in $Na_nBa_{14}CaN_6$ (n = 14, 17, 21, or 22) could be visualized as six octahedral units of $[Ba_5CaN]$, condensed by face-sharing so that Ca is shared at the center of the cluster.[51,52] The octahedral unit of $[Ba_5CaN]$ is derived from $[Ba_6N]$, by replacing a Ba with a Ca. It has been suggested that N can be introduced into a Na melt by adding an alkaline earth to form AE_6N (AE = alkaline earth/Figure 6a), which greatly enhances the solubility of N. When M (M = metal other than alkaline earth) is also introduced to the melt, AE_5MN or AE_6MN may be formed. Replacing a Sr with a Ga in $[Sr_6N]$ will generate $[Sr_5GaN]$ (Figure 2a), and adding a Ga into Sr_6N will give $[Sr_6GaN]$ (Figure 7a). Further condensation forms $[Sr_{12}GaN_3]$ in Figure 2b or $[Sr_{12}GaN_3]$ in Figure 7b, by condensing three of them so that apical Ga is shared at the center. It is interesting to note that these two different entities have a different structure, even though they have the same stoichiometry. The only difference is whether they originated from $[Sr_5GaN]$ (face-sharing) or $[Sr_6GaN]$ (edge-sharing). Suggested condensation reactions to obtain these merged building blocks were provided in the figures. As several basic units combine into a condensed building block, via sharing their edges, corners, or faces, several metal cations are released. As far as N is available, it is suggested that the cations recombine into 6- or 7-fold starting units, such as $[Sr_5GaN]$, $[Sr_6GaN]$, or $[Sr_6N]$. Whether such hypothetical building blocks, $[Sr_{12}GaN_3]$, are isolated entities (reaction intermediates) in a Na melt is a challenging question that perhaps can be answered in the future.

At present we have a poor understanding of the single-crystal growth process in a Na melt. Obtaining new nitride compounds relies mostly on reasonable prediction based on scarce thermodynamic data.[53−55] Circumstantial evidence suggests that not only thermodynamics govern the formation of nitride compounds but also the kinetics. However, carrying out direct experimental measurements on a kinetic process in solid state crystal growth is not an easy subject, especially in a molten Na solvent. The hypothetical building blocks which were introduced above might provide some clue to plausible new nitride compounds.

Summary

Two new Sr-rich strontium gallium nitrides, Sr_3GaN_3 and Sr_6GaN_5, which were synthesized by the Na flux method,

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(42) Etourneau, J.; Portier, J. *J. Alloys Compd.* **1992**, *188*, 1.
(43) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.
(44) O'Keeffe, M.; Brese, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 3226.
(45) Snyder, G. J.; Simon, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 689.
(46) Rauch, P. E.; Simon, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1519.
(47) Snyder, G. J.; Simon, A. *J. Am. Chem. Soc.* **1995**, *117*, 1996.
(48) Cordier, G.; Rönninger, S. *Z. Naturforsch.* **1987**, *42B*, 825.
(49) Jäger, J.; Stahl, D.; Schmidt, P. C.; Kniep, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 709.
(50) Cordier, G.; Ludwig, M.; Stahl, D.; Schmidt, P. C.; Kniep, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1761.
(51) Steinbrenner, U.; Simon, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 552.
(52) Simon, A.; Steinbrenner, U. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2117.
(53) Ranade, M. R.; Tessier, F.; Navrotsky, A.; Leppert, V. J.; Risbud, S. H.; DiSalvo, F. J.; Balkas, C. M. *J. Phys. Chem. B* **2000**, *104*, 4060.
(54) HcHale, J. M.; Navrotsky, A.; Kowach, G. R.; Balbarin, V. E.; DiSalvo, F. J. *Chem. Mater.* **1997**, *9*, 1538.
(55) McHale, J. M.; Navrotsky, A.; DiSalvo, F. J. *Chem. Mater.* **1999**, *11*, 1148.

contain planar nitridogallate anions, GaN_3^{6-} of D_{3h} symmetry. In both compounds, the GaN_3^{6-} anions are isolated from each other by surrounding countercations of Sr. The polyhedral perspective of their structure provides an interesting way to interpret the structure, which may allude to the way the single crystals grow. Sr_3GaN_3 was shown to be composed of only one kind of basic polyhedral unit: pseudo-octahedral [Sr_5-GaN]. Similarly, Sr_6GaN_5 was shown to consist of two kinds of basic polyhedral units: pseudo-octahedral [Sr_6N] and monocapped trigonal prismatic [Sr_6GaN]. By condensing three of the Ga-containing units into one, highly charged building blocks, [$Sr_{12}GaN_3$], could be imagined, and the structure of both crystals could be understood as a further condensation of the building blocks generated from these polyhedral units. The polyhedral perspective of these structures provides an interesting way to interpret the structure, which may allude to the way the single crystals grow.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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