Synthesis and Structure of One-, Two-, and Three-Dimensional Alkaline Earth Metal Gallium Nitrides: $Sr_3Ga_2N_4$, $Ca_3Ga_2N_4$, and $Sr_3Ga_3N_5$

S. J. Clarke[†] **and F. J. DiSalvo***

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

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We report the structures of three new alkaline earth metal gallium nitrides synthesized as crystals from the elements in sealed Nb tubes at 760 °C using Na/Sr and Na/Ca melts as growth media. The materials are all transparent insulators. Yellow $Sr_3Ga_2N_4$ is isostructural with the previously reported $Ba_3Ga_2N_4$ and $Sr_3Al_2N_4$. It crystallizes in *Pnna* (No. 52) with $a = 5.9552(6)$ Å, $b = 10.2753(8)$ Å, $c = 9.5595(9)$ Å, and $Z = 4$. It contains infinite chains, $^{1}_{\infty}[GaN_{4/2}{}^{3-}]$, of *trans*-edge-shared tetrahedra extending along the *b* axis. Colorless $Ca_3Ga_2N_4$ is isostructural with $Ca_3Al_2As_4$ and γ-$Ca_3Al_2N_4$. It crystallizes in *C*2/*c* (No. 15) with $a = 10.6901(11)$ Å, $b = 8.3655(7)$ Å, $c = 5.5701(4)$ Å, $\beta = 91.194(6)°$, and $Z = 4$. It contains infinite sheets, $^{2}_{\infty}[GaN_{4/2}{}^{3-}]$, of edge- and corner-sharing tetrahedra in the *bc* plane. Orange-yellow $Sr_3Ga_3N_5$ has a new structure; it crystallizes in $P\bar{1}$ (No. 2) with $a = 5.9358(6)$ Å, $b = 7.2383(8)$ Å, $c = 8.6853(12)$ Å, $\alpha = 108.332(10)°$, $\beta = 103.783(9)°$, $\gamma = 95.326(8)°$, and $Z = 2$. It is one of the few materials prepared from Na melts which has an infinite three-dimensional framework structure. It contains a $^{3}_{\infty}[Ga_3N_5{}^{6-}]$ framework of edge- and corner-sharing GaN_4 tetrahedra.

Introduction

Several binary nitrides, such as GaN, Si_3N_4, and AlN, are technologically useful. However, the chemistry of ternary nitrides has largely been neglected until recently. The main reason for this is that the synthesis of such materials is more difficult than that of the analogous oxides, sulfides, halides, or phosphides as summarized elsewhere.[1,2] The presence of electropositive metals in ternary nitrides helps to stabilize the nitride ion by inductive donation of electrons;[3] however, this often renders such nitrides very air-sensitive. We have been investigating ternary nitrides containing alkaline earth metals and later main group metals in order to assess the range of structures exhibited by these compounds, and their relation to other classes of materials such as oxides, sulfides, and phosphides.

Techniques for ternary nitride synthesis are summarized in refs 1 and 2. We focus on the use of Na/AE (AE = Ca, Sr, Ba) melts as growth media for alkaline earth metal containing nitrides, and have used this route in the synthesis of many new phases.[4−10] Species such as AE_6N are presumably responsible for introducing N into the melt.[11−13] In these reactions the alkaline earth elements are always incorporated into the products, often as the major constituent. Also, the other metal or non-metal, M, usually forms discrete $M_xN_y{}^{z-}$ nitridometallate units.

Experimental Section

Synthesis. All materials were handled in an MBraun MB 150M drybox in which the argon atmosphere was constantly circulated through molecular sieves and a Dow Q-5 Reagent copper catalyzer, and in which the combined O_2 and H_2O content was below 1 ppm. Then 8 cm long Nb tubes with a wall thickness of 0.5 mm and an internal diameter of 8 mm were cleaned using a mixture of 15% HF, 40% concentrated HNO_3 and 45% concentrated H_2SO_4. Starting materials were NaN_3 (Aldrich Chemical Co., 99%), Na (Aldrich Chemical Co., 99%), Sr (Aldrich Chemical Co., 99+%), Ca (Aldrich Chemical Co., 99+%) and Ga (Cerac 99.999%). The two strontium gallium nitrides may be prepared from the same reaction mixture, and one can adjust their ratio by appropriate adjustment of the Sr:Ga ratio. However it has not yet proved possible to synthesize either material exclusive of the other. In a typical reaction, reaction 1, which produced both of these phases in approximately equal abundance, the following amounts of reactants were placed in the tube: NaN_3 (81 mg), Na (54 mg), Sr (20 mg), and Ga (11 mg) so that the molar ratio Na:Sr:Ga:N was about 20:1.4:1:22. In the synthesis of $Ca_3Ga_2N_4$, reaction 2, the reactants were: NaN_3 (80 mg), Na (50 mg), Ca (10 mg), and Ga (15 mg) so that the molar ratio Na:Ca:Ga:N was about 15:1.2:1:17. The Nb tubes were sealed under 1 atm of clean Ar in a Centorr Associates arc furnace, taking care that the NaN_3 was not allowed to reach its decomposition temperature. The Nb tubes were then sealed inside quartz tubes under vacuum to prevent oxidation at elevated temperatures and placed upright in a muffle furnace. The temperature was raised to 760 °C over 15 h, maintained at 760 °C for 24 h, and then lowered linearly to 100 °C over 200 h, whereupon the furnace was turned off. The tubes were cut open using a tube cutter so that no Nb chips were produced, which could have contaminated the products. The part of the Nb tube containing the sample was washed anaerobically with anhydrous liquid ammonia to remove the Na and any excess alkaline earth metal, and the sample was then dried for several hours under vacuum. The bulk of the crystals could then be poured freely from the tube, although some material was stuck to the sides.

Elemental Analysis. The approximate ratio of the heavy elements (Na or heavier) was determined using the energy dispersive analysis

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[†] Current address: Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, U.K.

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Table 1. Crystallographic Data for $Sr_3Ga_2N_4$, $Ca_3Ga_2N_4$, and $Sr_3Ga_3N_5$

	$Sr_3Ga_2N_4$	$Ca_3Ga_2N_4$	$Sr_3Ga_3N_5$
fw	458.3	315.7	542.1
space group	*Pnna* (No. 52)	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
a/Å	5.9552(6)	10.6901(11)	5.9358(6)
b/Å	10.2753(8)	8.3655(7)	7.2383(8)
c/Å	9.5595(9)	5.5701(4)	8.6853(12)
α/deg	90	90	108.33(1)
β/deg	90	91.194(6)	103.78(1)
γ/deg	90	90	95.33(1)
V/Å^3	585.0(1)	498.0(1)	338.3(1)
Z	4	4	2
D (calcd)/g cm^{-3}	5.204(1)	4.211(1)	5.322(1)
T/K	295	295	295
wavelength/Å	0.710 69 (Mo Kα)	0.710 69 (Mo Kα)	0.710 69 (Mo Kα)
Abs. coeff/mm^{-1}	36.2	13.8	35.2
max, min transm	0.19, 0.035	0.62, 0.39	0.12, 0.0013
R1^a	0.033	0.020	0.044
R_w^{b}	0.059	0.042	0.102

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^2)^2]^{1/2}$, where $w = 1/[\sigma(F_o^2)^2 + (gP)^2]$, $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$, and $g = 0.0221$ for $Sr_3Ga_2N_4$, 0.0139 for $Ca_3Ga_2N_4$, and 0.0706 for $Sr_3Ga_3N_5$.

of X-rays (EDAX) method on a JEOL 733 Superprobe instrument equipped with software for standardless quantitative analysis. This technique could not be used to determine the N content of the materials because the X-rays produced from N are absorbed by the Be window of the detector.

Crystal Structure Determination. Crystals for single-crystal X-ray diffraction were mounted using 5-min epoxy cement on thin glass fibers inside dry glass capillary tubes which were sealed in the drybox using a hot Pt wire. Diffraction data were collected using a Siemens P4 four-circle diffractometer and Mo Kα radiation ($\lambda = 0.710\ 73$ Å) with a graphite monochromator. Accurate cell dimensions were determined from between 35 and 40 well-centered reflections using a least squares procedure. Data were collected using the Siemens XSCANS software.[14] During data collection the intensities of three strong reflections were measured every 100 reflections; they were observed not to change their intensities significantly, indicating that the crystals did not decompose or move during data collection. The intensity data were reduced by profile analysis and corrected for Lorentz−polarization and absorption effects. Scattering factors and anomalous dispersion terms were obtained from standard tables[15] internal to the software. Absorption corrections on all three crystals were carried out by face indexing because this was found to be much more satisfactory than using a ψ-scan, especially when the strongly absorbing Sr was present. Refinements carried out using ψ-scan corrected data had R factors and estimated standard deviations for the atomic parameters which were at least double those obtained when analytically corrected data were used. However, the positions of the atoms were the same within their standard deviations irrespective of the method employed for the absorption correction. Structure determination by direct methods and structure refinement using a nonlinear full-matrix least-squares minimization of the goodness of fit to F_o^2 was carried out using the SHELXTL version 5 suite.[16] An extinction correction was applied during the refinements.

Results

The product of reaction 1 was a yellow powder. When inspected using an optical microscope, it was clear that the sample contained two types of clear yellow crystals. One, $Sr_3Ga_2N_4$, was present as plates up to 1 mm in dimension, and the other, $Sr_3Ga_3N_5$, which was more orange in color, was present as fairly spherical faceted blocks. EDAX analysis on a few crystals of each type indicated that the Sr:Ga ratio was 1.21 ± 0.08:1 in the former case and 0.85 ± 0.05:1 in the latter case. No Na or other elements were detected in this experiment. The only other previously reported compound containing Sr, Ga, and N is black Sr_6NGa_5.[17] An interesting point is that $Sr_3Ga_2N_4$ is, like most nitrides of this type, very air-sensitive and rapidly decomposes, producing ammonia, while $Sr_3Ga_3N_5$ is stable in air for several days. This fact enables the materials to be easily distinguished. Automatic indexing of the reflections measured using single-crystal diffraction confirmed that the two materials were new phases and suggested that the platy material, $Sr_3Ge_2N_4$, is isostructural with $Ba_3Ga_2N_4$[9] and $Sr_3Al_2N_4$.[18] The product of reaction 2 contained a large number of air-sensitive colorless crystals up to 0.1 mm in dimension together with some dark powder which could not be identified using X-ray powder diffraction. EDAX analysis of the colorless crystals indicated that the Ca:Ga ratio was 1.1(1):1. Many calcium gallium nitrides have been reported previously;[19−22] however, only CaGaN[19] has a similar Ca:Ga ratio and is black and conducting. Automatic indexing of the reflections measured using single-crystal diffraction confirmed that this was a new phase and the structure solution revealed that it had the stoichiometry $Ca_3Ga_2N_4$. A third reaction in which both Ca and Sr were included in similar proportions produced mostly $Sr_3Ga_3N_5$ and $Ca_3Ga_2N_4$ with no evidence for any phases containing both Ca and Sr. The crystallographic information for all three phases is presented in Table 1.

1-D Crystal Structure of $Sr_3Ga_2N_4$. The crystal used was a thin plate, the large faces of which had a distorted hexagonal shape. The crystal dimensions were approximately 0.2 × 0.25 × 0.03 mm. One quarter sphere of data was collected with the following index limits: $-6 \le h \le +6$; $-1 \le k \le +10$ and $-1 \le l \le +11$ and a maximum 2θ of 48°. The absorption correction was carried out by indexing and measuring the faces of the crystal. The systematic extinctions suggested the space group *Pnna*, the same as in $Ba_3Ga_2N_4$[9] and $Sr_3Al_2N_4$.[18]

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Table 2. Atomic Parameters for $Sr_3Ga_2N_4$

atom	site	x	y	z	U_{eq}[a]
Sr1	8*e*	0.1105(1)	0.3450(1)	0.9132(1)	10.1(2)
Sr2	4*c*	0.25	0	0.9032(1)	10.4(3)
Ga1	4*c*	0.25	0	0.2289(1)	7.2(3)
Ga2	4*d*	0.1612(1)	0.25	0.25	7.1(3)
N1	8*e*	0.3756(9)	0.1474(5)	0.1239(6)	9(1)
N2	8*e*	0.0071(9)	0.0951(5)	0.3323(5)	9(1)

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

Table 3. Atomic Separations (Å) and Bond Angles (deg) in $Sr_3Ga_2N_4$[a]

Ga1−N1	1.965(6)[2]	Ga2−N1	2.048(5)[2]
Ga1−N2	2.006(5)[2]	Ga2−N2	1.999(5)[2]
N1−Ga1−N1	118.6(3)	N1−Ga2−N1	102.9(3)
N1−Ga1−N2	98.7(2)[2]	N1−Ga2−N2	96.2(2)[2]
N1−Ga1−N2	110.7(2)[2]	N1−Ga2−N2	117.7(2)[2]
N2−Ga1−N2	121.0(3)	N2−Ga2−N2	125.3(3)
Sr1−N1	2.491(5)	Sr2−N1	2.703(5)[2]
Sr1−N2	2.561(6)	Sr2−N1	2.708(5)[2]
Sr1−N2	2.584(5)	Sr2−N2	2.893(5)[2]
Sr1−N2	2.773(5)		
Sr1−N1	3.100(5)		
Sr1−N1	3.267(6)		

[a] The numbers in square brackets designate the number of symmetry equivalent bonds or angles.

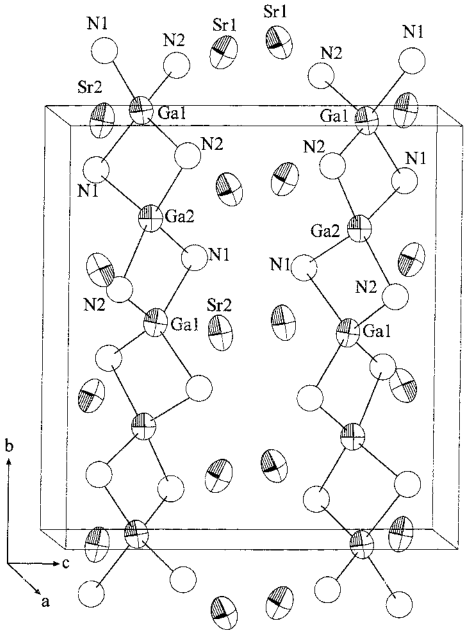

Figure 1. Crystal structure of $Sr_3Ga_2N_4$ showing the Ga−N bonding. The thermal ellipsoids are shown at the 99% level. N atoms were refined isotropically and are shown as spheres.

Structure solution for the heavy atoms by direct methods produced a starting model from which the nitrogen positions were immediately obvious from the difference Fourier map, during the early stages of the refinement. This confirmed that the material is isostructural with $Ba_3Ga_2N_4$[9] and $Sr_3Al_2N_4$.[18] Refinement in *Pnna* produced a final R1 of 3.3% and a wR2 of 5.9% for all data, with a data to parameter ratio of 14:1. The atomic parameters are summarized in Table 2, and selected interatomic distances and bond angles are given in Table 3.

The structure of $Sr_3Ga_2N_4$ is shown in Figure 1, which includes an anisotropic representation of the heavy atoms with the major axes proportional to the diagonal elements of the orthogonalized vibration tensor. $^1_\infty[GaN_{4/2}{}^{3-}]$ chains of edge-linked tetrahedra extend along the *b* axis. Ga−N distances range from 1.965(6) to 2.048(5) Å, which are very similar to the distances in $Ba_3Ga_2N_4$,[9] and quite similar to those of about 1.94 Å found in hexagonal GaN[23] and 1.95 Å in Li_3GaN_2[24] in which Ga is in a regular tetrahedral environment. The average N−Ga−N angles in $Sr_3Ga_2N_4$ are about 98° if the two N atoms are in the same bridge and about 115° if the N atoms are in different bridges. The angular distortion of the tetrahedra presumably arises from Ga−Ga repulsion and is similar to that found in $Ba_3Ga_2N_4$, although the reason for the large variation in bond lengths is not clear. Ga1 and Ga2 alternate in each chain, and their separation is a short 2.630(1) Å which is actually shorter than the separation in elemental Ga (2.71 Å).[25] The edge sharing of tetrahedra never occurs in gallium oxide chemistry, but is relatively common in nitrides and is even found to occur in the case of silicon in $Ba_5Si_2N_6$,[4] where $Si_2N_6{}^{10-}$ units are composed of a pair of edge-sharing tetrahedra. Another nitride which shows this type of infinite chain, apart from those which are isostructural with $Sr_3Ga_2N_4$, is Li_3FeN_2.[26] The propensity for these edge-sharing motifs to occur in nitrides presumably arises from the more covalent nature of the materials when compared to oxides. Edge sharing also occurs in the $Ga_2P_6{}^{12-}$ units present in $Ba_6Ga_2P_6$;[27] similar infinite chains to those described here occur, for example, in SiS_2 and $SiSe_2$[28] and in $KFeS_2$[29] and are even reported to occur in an unusual fibrous modification of SiO_2.[30]

2-D Crystal Structure of $Ca_3Ga_2N_4$. One hemisphere of data was collected with the following index limits: $-1 \le h \le +11$; $-8 \le k \le +8$ and $-5 \le l \le +5$, and a maximum 2θ of 45°. The systematic extinctions suggested the space group *C*2/*c*. The absorption correction was carried out by indexing the faces of the parallelepiped. Structure solution for the heavy atoms by direct methods revealed that the true Ca:Ga ratio was 3:2 and thus larger than the ratio determined by standardless EDAX. The nitrogen atoms were located during the early stages of nonlinear least-squares refinement, and it was clear that the material is isostructural with $Ca_3Al_2As_4$[31] and with the γ polymorph of $Ca_3Al_2N_4$.[32] Refinement in *C*2/*c* produced a final R1 of 2.0% and a *wR2* of 4.2% for all data. There were sufficient data in this case for the N atoms to be refined anisotropically and maintain a data to parameter ratio greater than 10:1. The atomic parameters were standardized using STRUCTURE TIDY,[33] and are given in Table 4, where comparison with the published setting of $Ca_3Al_2As_4$[31] is also given. Selected interatomic distances and bond angles are given in Table 5.

The structure of this material is shown in Figures 2 and 3. $^2_\infty[GaN_{4/2}{}^{3-}]$ sheets are constructed from Ga_2N_6 units which are composed of a pair of edge sharing tetrahedra. These units are each linked to four others via the corners which are not involved in the edge sharing. Thus half the N atoms participate in edge sharing (N1) and the other half participate in corner sharing

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Table 4. Atomic Parameters[a] for $Ca_3Ga_2N_4$ As Given by STRUCTURE TIDY[33]

atom	site	x	y	z	U_{eq}[b]
Ca1	8*f*	0.11609(6) [0.11609]	0.13531(8) [0.13531]	0.5419(1) [0.4581]	8.9(2)
Ca2	4*e*	0 [0]	0.3992(1) [0.1008]	0.25 [0.25]	6.9(2)
Ga1	8*f*	0.29721(3) [0.20279]	0.11910(4) [0.38090]	0.09431(6) [0.09431]	5.5(2)
N1	8*f*	0.1177(3) [0.3823]	0.1749(3) [0.3251]	0.0209(5) [0.0209]	8.0(6)
N2	8*f*	0.3426(3) [0.8426]	0.0809(3) [0.4191]	0.4320(5) [0.0680]	7.3(6)

[a] The numbers in square brackets denote the values corresponding to the setting of the isostructural $Ca_3Al_2As_4$.[31] [b] The equivalent isotropic thermal displacement parameter, U_{eq} in Å^3 × 10^3 is defined as one third of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor.

Table 5. The Atomic Separations (Å) and Bond Angles (deg) in $Ca_3Ga_2N_4$

Ga1−N1	2.009(3)	Ga1−N1	2.058(3)
Ga1−N2	1.959(3)	Ga1−N2	1.967(3)
N2−Ga1−N2	104.1(1)	N2−Ga1−N1	116.8(1)
N2−Ga1−N1	109.5(1)	N2−Ga1−N1	110.4(1)
N2−Ga1−N1	117.0(1)	N1−Ga−N1	99.7(1)
Ca1−N2	2.419(3)	Ca1−N1	2.538(3)
Ca1−N2	2.551(3)	Ca1−N1	2.598(3)
Ca1−N1	2.688(3)	Ca1−N1	2.921(3)
Ca2−N2	2.423(3) [2]	Ca2−N2	2.498(3) [2]
Ca2−N1	2.607(3) [2]		

(N2). All N atoms are bonded to two Ga atoms, all of which are crystallographically equivalent. The Ga−N bonds in the edge-shared bridges are at least 0.05 Å longer than those in the corner-shared bridges; the latter are similar in length to those in GaN[23] and Li_3GaN_2,[24] which contain only corner-linked GaN_4 tetrahedra. The N1−Ga−N1 angles in the edge-shared bridges are 99.7(1)° which is considerably less than the ideal tetrahedral angle. The angular degree of tetrahedral distortion is similar to that in $Sr_3Ga_2N_4$ and the isostructural $Ca_3Al_2As_4$[31] and γ-$Ca_3Al_2N_4$.[32] In $Ca_3Ga_2N_4$ one can rationalize all the tetrahedral distortion in terms of Ga−Ga repulsion across the short Ga−Ga distance of 2.622(1) Å. Both Ca atoms are octahedrally coordinated by N. The Ca1 octahedra share edges with each other and faces with the Ca2 octahedra. The Ca2 octahedra share edges with each other. N1 is seven-coordinate (two Ga and five Ca) and N2 is in a roughly octahedral coordination (two Ga and four Ca). One of the Ca1−N1 distances is fairly long: 2.921(3) Å.

3-D Crystal Structure of $Sr_3Ga_3N_5$. The use of $Sr_3Ga_2N_4$ as an EDAX standard indicated that the Sr:Ga ratio in the second product from reaction 1 was probably 1:1. A crystal with dimensions 0.17 × 0.16 × 0.07 mm was used, and a full sphere of data was collected with the following index limits: $-6 \le h \le +6$; $-7 \le k \le +7$ and $-9 \le l \le +9$, and a maximum 2θ of 45°. There were no systematic extinctions in the diffraction data, and the values of the cell parameters indicated that the unit cell was triclinic. The absorption correction was carried out by face indexing, and structure solution by direct methods in $P\bar{1}$ allowed the heavy atoms to be found. The N atoms were then easily located from the difference Fourier map during the initial stages of nonlinear least-squares refinement. This confirmed that the stoichiometry was $Sr_3Ga_3N_5$. Refinement on data corrected for absorption by measurement of the faces of the roughly hexagonal prismatic crystal produced a final R1 of 4.3% and wR2 of 10.1% for all data with a data to parameter ratio of 12:1. The relatively high R factors are probably a consequence of the difficulty of performing the absorption correction, either analytically or using a ψ-scan on such a highly absorbing crystal. The atomic coordinates were standardized using the program STRUCTURE TIDY[33] and are presented in Table 6. Selected interatomic distances and bond angles are given in Table 7.

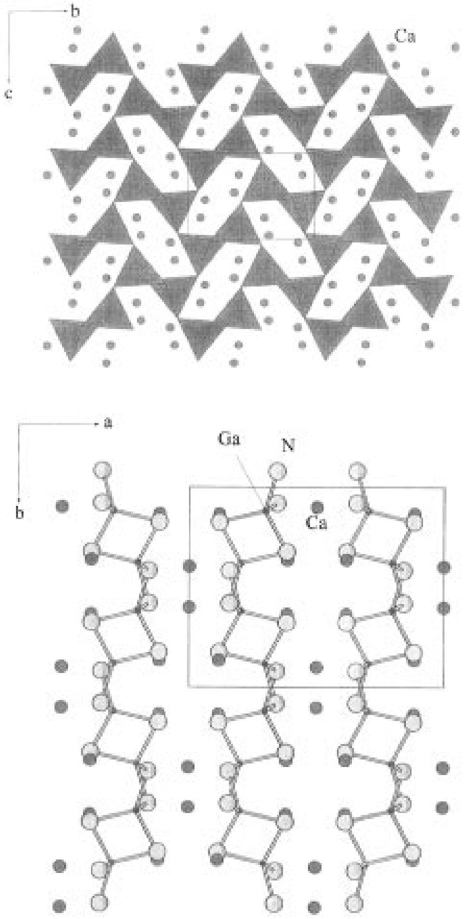

Figure 2. Representations of the layered crystal structure of $Ca_3Ga_2N_4$: (a, top) polyhedral representation of the $^2_\infty[GaN_{4/2}{}^{3-}]$ sheets; (b, bottom) edge-on view of the sheets showing Ga−N bonds.

The structure, shown in Figures 4 and 5, consists of two basic structural units. Linear Ga_4N_{10} units are formed from four GaN_4 tetrahedra which are *trans*-edge-linked, i.e. they can be thought of as fragments of the infinite chains in $Sr_3Ga_2N_4$, or as edge-linked pairs of the Ga_2N_6 units found in $Ca_3Ga_2N_4$. The structure also contains Ga_2N_6 units. The Ga_4N_{10} units are corner linked to one another at their ends in overlapping fashion, and they form ribbons which extend along the a axis. These ribbons are joined in the other two crystallographic directions via corner linking with the Ga_2N_6 units. Some N atoms are coordinated by three Ga; others, by just two. The Ga−N and Ga−Ga separations are very similar to those found in $Sr_3Ga_2N_4$ and $Ca_3Ga_2N_4$. The Ga−N distances are generally shorter when the bond participates in corner linking than when it participates in edge linking, although the situation is much less clear in this case than it is in $Ca_3Ga_2N_4$. The average Ga−N distance involving N atoms shared by three Ga atoms is 0.03 Å longer than that involving N atoms shared by just two Ga atoms. This may be a phenomenon similar to that of the lengthening of bridging bonds relative to terminal bonds in silicates,[34] which is ascribed to competition for bridging oxygen by the two silicon atoms bonded to it. This phenomenon also seems to occur in

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(34) Liebau, F. *Structural Chemistry of Silicates*; Springer-Verlag: Berlin, Germany, 1985.

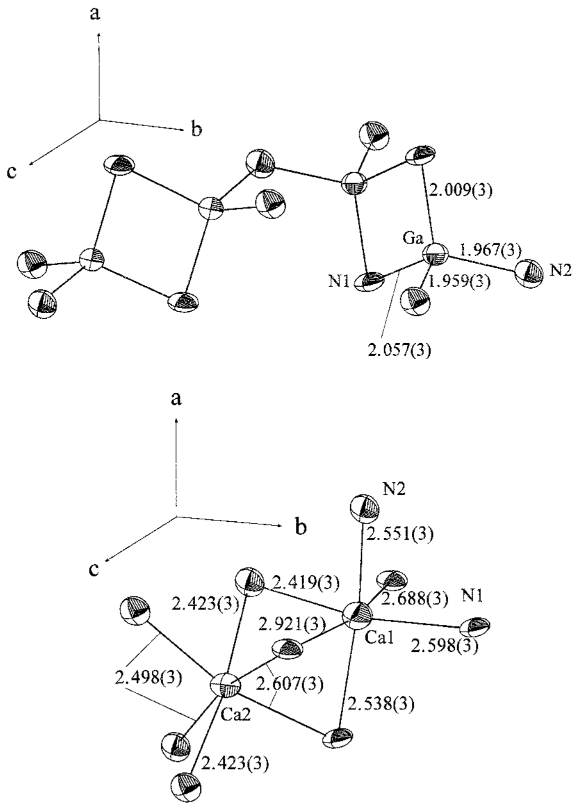

Figure 3. Coordination geometry of (a, top) the Ga atoms and (b, bottom) the Ca atoms in $Ca_3Ga_2N_4$. All atoms were refined anisotropically, and the ellipsoids are shown at the 99% level.

Table 6. Atomic Parameters for $Sr_3Ga_3N_5$ (All Atoms on the 8*i* Site)

atom	*x*	*y*	*z*	$U_{eq}{}^{a}$
Sr1	0.1830(2)	0.5879(2)	0.3919(1)	10.6(4)
Sr2	0.3306(2)	0.1391(2)	0.1264(1)	8.0(4)
Sr3	0.3438(2)	0.3452(2)	0.7982(1)	9.9(4)
Ga1	0.0919(2)	0.6840(2)	0.0272(1)	5.1(4)
Ga2	0.2904(2)	0.0443(2)	0.4310(1)	6.0(4)
Ga3	0.8772(2)	0.1217(2)	0.2844(1)	6.1(4)
N1	0.045(2)	0.892(1)	0.221(1)	9(2)
N2	0.165(2)	0.289(1)	0.475(1)	8(2)
N3	0.236(1)	0.476(1)	0.095(1)	4(2)
N4	0.615(2)	0.054(1)	0.382(1)	10(2)
N5	0.744(2)	0.223(1)	0.109(1)	8(2)

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

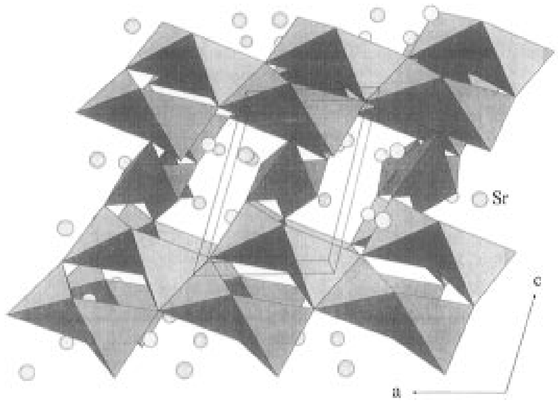

Figure 4. Crystal structure of $Sr_3Ga_3N_5$ viewed down the *b* axis. The condensation of the Ga_4N_{10} units is clearly shown; the Ga_2N_6 units join the ensuing ribbons and point into the page. Sr atoms are shown as spheres.

Table 7. Atomic Separations (Å) and Bond Angles (deg) in $Sr_3Ga_3N_5$

Ga1−N5	1.926(8)	Ga1−N3	1.977(9)
Ga1−N1	1.971(8)	Ga1−N3	2.016(9)
Ga2−N2	1.945(9)	Ga2−N1	1.959(9)
Ga2−N4	1.957(9)	Ga2−N4	2.068(9)
Ga3−N5	1.932(9)	Ga3−N2	2.029(9)
Ga3−N1	2.010(9)	Ga3−N4	2.033(9)
Ga1−Ga1	2.633(2)	Ga3−Ga2	2.677(2)
Ga2−Ga2	2.721(2)		
N1−Ga1−N5	115.2(4)	N5−Ga1−N3	111.2(4)
N1−Ga1−N3	112.2(3)	N5−Ga1−N3	115.9(4)
N1−Ga1−N3	103.4(3)	N3−Ga1−N3	97.5(3)
N2−Ga2−N4	117.8(4)	N4−Ga2−N1	123.1(4)
N2−Ga2−N1	96.5(4)	N4−Ga2−N4	95.0(3)
N2−Ga2−N4	116.8(4)	N1−Ga2−N4	108.8(3)
N5−Ga3−N1	116.9(3)	N1−Ga3−N2	92.3(4)
N5−Ga3−N2	118.7(4)	N1−Ga3−N4	110.8(4)
N5−Ga3−N4	107.7(4)	N2−Ga3−N4	109.8(3)
Sr1−N2	2.490(9)	Sr1−N2	2.688(9)
Sr1−N3	2.554(7)	Sr1−N1	3.094(9)
Sr1−N4	2.671(9)	Sr1−N5	3.376(10)
Sr2−N5	2.527(9)	Sr2−N4	2.723(10)
Sr2−N3	2.631(9)	Sr2−N1	2.783(8)
Sr2−N5	2.686(9)	Sr2−N1	3.221(9)
Sr2−N2	3.295(8)		
Sr3−N3	2.514(9)	Sr3−N2	2.639(9)
Sr3−N1	2.688(9)	Sr3−N3	2.705(7)
Sr3−N4	2.882(9)	Sr3−N5	3.100(9)

the framework ternary silicon nitrides which have been prepared.[35−38] For example in $Ca_2Si_5N_8$[36] the Si−N bonds involving N atoms shared by three Si atoms are, on average, 0.05(1) Å longer than those involving N atoms shared by two Si. The Sr atoms in $Sr_3Ga_3N_5$ occupy the cavities formed by the ${}^{3}_{\infty}[Ga_3N_5{}^{6-}]$ framework. Sr1 is 4 + 2 coordinated by N, Sr2 is 5 + 2 coordinated and Sr3 is 5 + 1 coordinated, although this latter is roughly octahedral. N1 is 5 + 2 coordinated by metals, N2 is 5 + 1 coordinated, N3 and N4 are 6 coordinated and N5 is 4 + 2 coordinated. The shortest Sr−N distances are about 2.5 Å. The more tenuous Sr−N bonds, given by the +*n* notation, are up to 3.3 Å in length, and are slightly longer than some of the Sr−Ga distances, which are close to 3.0 Å. The Sr atoms are anisotropic by up to 30%, although not all in the same crystallographic direction. This suggests that the anisotropy is a consequence of their irregular coordination spheres rather than merely due to the difficulty of performing the analytical absorption correction on such a multifaceted crystal. A full list of anisotropic thermal displacement parameters, U_{ij}, for the heavy atoms is available as Supporting Information.

Discussion

The structures of the three compounds discussed here should be contrasted with those of the silicates and the known silicon-containing ternary nitrides. Silicates are based on tetrahedral building blocks which are condensed together with bewildering variety, but always by the sharing of a tetrahedral corner with zero or one other. The silicon nitrides synthesized at temperatures in excess of 1500 °C in the group of Schnick include

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(35) Schlieper, T.; Milius, W.; Schnick, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1380.

(36) Schlieper, T.; Schnick, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1037.

(37) Schlieper, T.; Schnick, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1535.

(38) Woike, M.; Jeitschko, W. *Inorg. Chem.* **1995**, *34*, 5105.

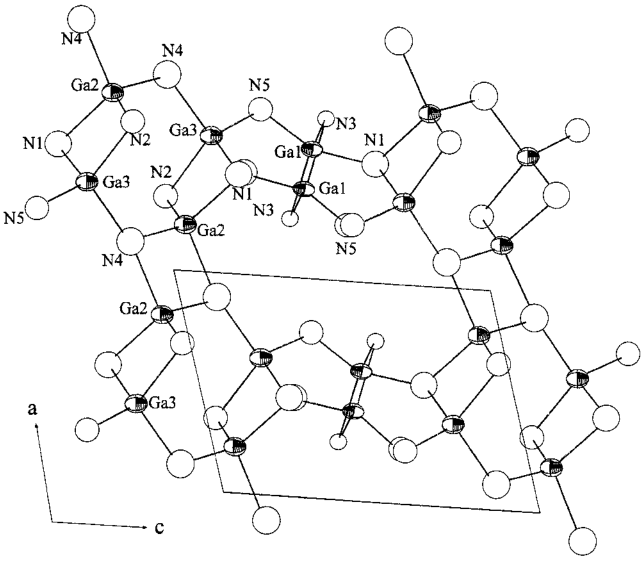

Figure 5. Ga−N bonding in $Sr_3Ga_3N_5$ showing the thermal ellipsoids at the 99% level. N atoms were refined isotropically and are shown as spheres; the Sr atoms have been removed for clarity. The *b* axis is perpendicular to the page.

$AE_2Si_5N_8$ (AE = Ca, Sr, Ba)[35,36] and $Ln_3Si_6N_{11}$,[37,38] and these are built up from SiN_4 tetrahedra sharing corners with up to two others. This apparently reflects the trivalency of nitrogen compared to the divalency of oxygen. The materials described in this article all have in common edge sharing of tetrahedra, which reflects the fact that nitrides are more covalent than oxides and can thus accommodate close approach of metals across a tetrahedral edge. In this respect, nitrides show more similarities with sulfides and the heavier pnictides than with oxides. The largest building block common to the three materials described here is the Ga_2N_6 unit composed of a pair of edge-sharing tetrahedra. Similar units are found isolated from one another in $Ba_5Si_2N_6$[4] which is formed under conditions similar to the phases discussed here. In the present cases, these units are condensed together either by further edge sharing, as in $Sr_3Ga_2N_4$, to form chains, by corner sharing, as in $Ca_3Ga_2N_4$, to form sheets, or by both, as in $Sr_3Ga_3N_5$, to form a framework.

The framework nitride $Cs_5[Na\{W_4N_{10}\}]$[39] has been synthesized from the reaction between $CsNH_2$, $NaNH_2$, and W in high-pressure autoclaves at 700 °C. This route is similar in principle to that described here, although the pressure of N_2 is greater (up to 300 atm) in the autoclaves. $Cs_5[Na\{W_4N_{10}\}]$ has a framework of corner-sharing WN_4 tetrahedra, and is the only framework ternary nitride apart from $Sr_3Ga_3N_5$ to have been synthesized by this relatively soft approach. It has been observed empirically that nitrides grown from a melt of electropositive metals usually contain discrete units composed of one or two polyhedra or infinite chains which are separated by the alkali or alkaline earth metal. However appropriate condensation of the species present in the melt, which in the cases discussed here may include GaN_x units, can also lead to nitrides with sheet and framework structures. In the case of $Sr_3Ga_3N_5$ the framework structure, which is partly a consequence of the relatively low alkaline earth metal content compared to most other alkaline earth metal ternary nitrides, results in kinetic stability to moist air, since it remains unaffected after several days. Most of the alkaline earth metal gallium nitrides synthesized previously contain Ga in a reduced oxidation state and with Ga−Ga bonds. These include $Ca_{18.5}Ga_8N_7$,[20] $Ca_5Ga_2N_4$,[21] CaGaN,[19] and AE_6NGa_5 (AE = Sr, Ba).[17] The compounds discussed here contain fully oxidized Ga in the expected tetrahedral coordination, rather than in the unusual trigonal coordination found in Ca_6GaN_5.[22] We have previously synthesized both reduced and fully oxidized alkaline earth metal germanium nitrides by this route,[10,40] and it seems reasonable to expect that reduced ternary gallium nitrides may also be attainable under similar conditions.

Ca and Sr have highly colored binary nitrides with modest charge transfer band gaps. GaN has a band gap of 3.4 eV and is colorless. It seems that the band structure of the weakly colored transparent materials considered here results from a lowering in energy of the N valence band by participation in strongly covalent Ga−N bonding, resulting in band gaps intermediate between those of alkaline earth metal nitrides and those of GaN.

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Supporting Information Available: Three X-ray crystallographic files in CIF format are available. Access ordering information is given on any current masthead page.

IC9612562

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(39) Niewa, R.; Jacobs, H. *Z. Anorg. Allg. Chem.* **1996**, *622*, 881.

(40) Clarke, S. J.; DiSalvo, F. J. Submitted for publication in *Inorg. Chem.*