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Synthesis and Structure of Two New Strontium Germanium Nitrides: $Sr_3Ge_2N_2$ and Sr_2GeN_2

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We report the structures of two new strontium germanium nitrides synthesized as crystals from the elements in sealed Nb tubes at 750 °C using liquid Na as a growth medium. $Sr_3Ge_2N_2$ is isostructural with the previously reported Ba analogue. It crystallizes in $P2_1/m$ (No. 11), with $a = 9.032(2)$ Å, $b = 3.883(1)$ Å, $c = 9.648(2)$ Å and $\beta = 112.42(3)°$, and has two formula units per unit cell. It contains GeN_2^{4-} units and additionally $^{1}_{\infty}|Ge^{2-}$ zigzag chains. Sr_2GeN_2 crystallizes in $P4_2/mbc$ (No. 135) with $a = b = 11.773(2)$ Å and $c = 5.409(1)$ Å and has $Z = 8$. It also contains GeN_2^{4-} units which have 18 valence electrons and, consequently are bent, like the isoelectronic molecule SO_2.

Introduction

A number of binary nitrides have technological uses, and much research is directed toward the fabrication of GaN-based semiconductors or AlN and Si_3N_4 based ceramics, for example. The chemistry of ternary nitrides has been neglected until recently. The main reason for this is that the synthesis of such materials is much more difficult than that of the analogous oxides, sulfides, halides or phosphides. First, the strong bond in the N_2 molecule (941 kJ·mol^{-1} *cf.* 500 kJ·mol^{-1} for O_2) results in the fact that nitrides are thermodynamically unstable with respect to the formation of oxides and also that forcing conditions are often required when N_2 is used as the source of nitrogen. Many binary and ternary nitrides, once formed, are very susceptible to decomposition *via* reaction with atmospheric O_2 or, especially, H_2O. Some even decompose over time when kept in a drybox due to the presence of stray O_2 or H_2O. Binary and ternary nitrides containing electropositive metals are particularly air-sensitive, while many transition metal binary nitrides are stable in air even above room temperature as a result of slow oxidation kinetics. Decomposition of nitrides at elevated temperatures is also common, with reduction of the metal and release of N_2. For example, Ta_3N_5 decomposes to TaN at approximately 900 °C and eventually to Ta_2N at higher temperatures. Second, the large energy required to make N^{3-} anions from N atoms (2300 kJ·mol^{-1} *cf.* 700 kJ·mol^{-1} for O^{2-} from O or 331 kJ·mol^{-1} for S^{2-} from S) results in bonds that are considerably more covalent than in oxides, or even sulfides. It has been shown that electropositive metals, notably Li and the alkaline earths, stabilize transition and main group ternary nitrides by means of the inductive donation of their electrons.[1] Many of the materials formed in this way are very rich in the electropositive metal, and very air-sensitive; also they usually contain isolated MN_x^{n-} units rather than the extended framework structure required for metallic or other potentially technologically useful properties.

Techniques for ternary nitride synthesis include the following: (1) traditional ceramic reactions between binary nitrides; (2) softer routes such as the action of flowing NH_3 on oxides or intermetallic precursors;[2] (3) reactions at the interface of a transition metal and a molten alkaline-earth metal under an N_2 atmosphere; and (4) the use of Li_3N as a flux. In this paper we discuss a newer method: the use of liquid Na as a growth medium, or perhaps a true flux, for single crystals of alkaline earth containing nitrides. Our group has used this route to synthesize the following compounds: Sr_2NiN_2,[3] $Ba_5Si_2N_6$,[4] $Ba_3Ge_2N_2$,[5] Ba_2ZnN_2 and Sr_2ZnN_2,[6] Ba_3ZnN_2O,[7] SrCuN and $Sr_6Cu_3N_5$,[8] and $Ba_3Ga_2N_4$.[9]

In these reactions Na, NaN_3 and an alkaline earth metal are sealed in a Nb, Ta or stainless steel tube, together with a metal or non-metal, M. The tubes are heated to a temperature of between 700 and 1000 °C and then cooled slowly to room temperature. NaN_3 decomposes to Na and N_2 at 300 °C and is the source of nitrogen. Na is typically present in a 5- to 50-fold molar excess over the species M. Crucially, Na does not form a stable binary nitride; also it is observed that it is not usually incorporated into the products. The excess Na is easily removed by washing the products with liquid ammonia under anaerobic conditions. In most cases Nb from the tube is not included in the products. An empirical observation in these reactions is that large crystals may be formed when the heavier alkaline earths are present, and these elements are always incorporated into the products, often as the major constituent. Also the other metal or non-metal forms discrete $M_xN_y^{z-}$ units. For example the compounds listed above contain NiN_2^{4-},[3] $Si_2N_6^{10-}$,[4] GeN_2^{4-},[5] ZnN_2^{4-},[6] $^{1}_{\infty}|CuN_{2/2}^{2-}$,[8] CuN_2^{5-} and $Cu_2N_3^{7-}$,[8] and $^{1}_{\infty}|GaN_{4/2}^{3-}$ [9] units, respectively. The nature of the reactions in a Na flux has been elucidated to some extent by the results of A. Simon *et al.* who isolated the subnitrides Na_5Ba_3N,[10] $NaBa_3N$[11] and $Na_{16}Ba_6N$[12] and showed that they melt at temperatures below 200 °C. The solid state structures all include the N-centered octahedral Ba_6N unit, and this species is presumably responsible for introducing N into the solution. Note that in reactions in which the alkaline earth metal is not included, a Na−M intermetallic is sometimes produced rather

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than a binary nitride. Another empirical observation is that these reactions are most successful when elemental reactants are used as starting materials[13] rather than binary nitrides. We surmise that the elements dissolve in Na and then react to produce a possibly insoluble nitride.

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. A 10 cm long Nb tube with a wall thickness of 1 mm and an internal diameter of 7 mm was 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+%) and Ge (Cerac 99.999%) which was obtained as chunks and ground to −300 mesh. Two reaction mixtures were prepared. In reaction 1, which produced $Sr_3Ge_2N_2$, the following amounts of reactants were placed in the tube: NaN_3 (69.6 mg), Na (52.4 mg), Sr (36.0 mg), and Ge (21.3 mg) so that the molar ratio Na:Sr:Ge:N was 11.6:1.4:1.0:11.1. In reaction 2, which produced Sr_2GeN_2, the contents were NaN_3 (71.5 mg), Na (60.0 mg), Sr (20.5 mg), and Ge (8.8 mg) so that the molar ratio Na:Sr:Ge:N was 30.9:1.9:1.0:27.5. 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 sealed under vacuum in quartz tubes to prevent oxidation at elevated temperatures and placed upright in a muffle furnace. The temperature was raised to 750 °C over 12 h, maintained at 750 °C for 12 h and then lowered linearly to 100 °C over 200 h, whence 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 samples were washed anaerobically with anhydrous liquid ammonia to remove the Na and any excess Sr and then dried under vacuum.

X-ray Powder Diffraction. Powder diffraction data of ground portions of the samples were collected using a Scintag XDS 2000 diffractometer operating in Bragg−Brentano geometry. The samples were covered with a mylar film to prevent aerial oxidation.

Elemental Analysis. The approximate ratio of the heavy elements (Na or heavier) was determined using energy dispersive analysis of X-rays (EDAX) analysis using a JEOL 733 Superprobe instrument. 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 in dry glass capillary tubes which were sealed inside the dry box using a hot Pt wire. Diffraction data were collected using a Siemens P4 four-circle diffractometer and Mo $K\alpha$ radiation (λ = 0.71073 Å) with a graphite monochromator. Accurate cell dimensions were determined using about 35 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 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. Absorption corrections were found to be crucial in these crystals because both Ge and Sr are very strong absorbers of Mo $K\alpha$ radiation. The corrections were carried out either using ψ-scans or, where possible, an analytical correction derived from the morphology of the crystal, as described in the Supporting Information. 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.[15] An extinction correction was applied during the refinements.

Table 1. Crystallographic Data for $Sr_3Ge_2N_2$ and Sr_2GeN_2

formula	$Sr_3Ge_2N_2$	Sr_2GeN_2
fw	436.1	275.9
space group	$P2_1/m$	$P4_2/mbc$
a/Å	9.032(2)	11.773(2)
b/Å	3.883(1)	
c/Å	9.648(2)	5.409(1)
β/deg	112.42(3)	
V/Å^3	312.9(3)	749.7(3)
Z	2	8
D(calcd)/g cm^{-3}	4.630(3)	4.888(2)
temp/K	295	295
wavelength/Å	0.71069 (Mo$K\alpha$)	0.71069 (Mo$K\alpha$)
abs coeff/mm^{-1}	36.09	34.78
max, min transm	0.48, 0.03	0.08, 0.03
$R1^a$	0.1058	0.0381
$R_w{}^b$	0.2487	0.0527

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$, where $w = 1/[\sigma(F_o^2)^2 + (gP)^2]$; $P = (\max(F_o^2,0) + 2F_c^2)/3$; $g = 0.2123$ for $Sr_3Ge_2N_2$ and 0.0075 for Sr_2GeN_2.

Results and Discussion

The products of both reactions appeared superficially to be the same: dark blue-gray powders. When inspected using an optical microscope, it was clear that both products contained crystals but with a different habit in each case. In reaction 1 ($Sr_3Ge_2N_2$), the crystals were small needles about 0.1 mm long and were prone to aggregation. In reaction 2 (Sr_2GeN_2), the crystals were up to 0.2 mm long and in the form of rectangular prismatic blocks. EDAX analysis on a few crystals from each reaction indicated that the Sr:Ge ratio in reaction 1 was between 1.5:1 and 1.2:1, and that the ratio in reaction 2 was between 2.0:1 and 1.6:1. The different ratios are compatible with the different ratios of these two elements in the starting materials, and the uncertainty in the ratios is typical for this technique. No Na was detected in this experiment. The X-ray powder diffraction patterns of both products were complex, different from one another and did not match with any known patterns. The EDAX and powder diffraction experiments did not suggest that there was significant contamination of one phase by the other. In both cases, samples exposed to air for a few minutes decomposed to produce a yellow powder, which was not characterized, and NH_3 gas indicating that both materials are nitrides.

Automatic indexing of the reflections measured using single crystal diffraction indicated that the crystals from the two different reactions had different unit cells. This information is presented in Table 1.

Crystal Structure of $Sr_3Ge_2N_2$. It was not possible to index the faces of the crystal due to its irregular shape, so the absorption correction was carried out using a ψ-scan in which 41 reflections were measured in 18 different orientations of the crystal. Systematic extinctions suggested $P2_1$ or $P2_1/m$ as possible space groups. We chose the highest symmetry space group, $P2_1/m$, and, using direct methods, obtained a model for the Sr and Ge atoms which was isostructural with $Ba_3Ge_2N_2$.[5] The N atoms were located during the initial stages of least squares refinement, and the structural analysis indicated that the true Sr:Ge:N ratio was 3:2:2; i.e., at the high end of the range suggested by EDAX analysis. This structure refined successfully to give a final R-factor (defined as $R1$ in

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Table 2. Atomic Parameters for $Sr_3Ge_2N_2$[a]

atom	x	y	z	U_{eq}[b]
Sr(1)	0.3165(2)	$^1/_4$	0.9442(3)	26(1)
Sr(2)	0.5202(3)	$^1/_4$	0.6701(3)	26(1)
Sr(3)	0.1175(4)	$^1/_4$	0.3522(3)	27(1)
Ge(1)	0.7580(4)	$^1/_4$	0.3485(3)	26(1)
Ge(2)	0.9155(4)	$^1/_4$	0.9441(3)	28(1)
N(1)	0.6804(34)	$^1/_4$	0.5108(26)	39(6)
N(2)	0.5733(32)	$^1/_4$	0.1784(24)	34(6)

[a] There is considerable uncertainty in the location of the N atoms which arises from absorption effects which hamper the structure refinement. [b] 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 $\mathbf{U}_{ij}$ tensor.

SHELXTL) of 10.6%. This large value may be due to shortcomings of the ψ-scan absorption correction. There was no indication that the true symmetry is lower than $P2_1/m$. Even at this level of refinement, it is clear that the composition of this material is $Sr_3Ge_2N_2$ and it is isostructural with $Ba_3Ge_2N_2$.[5] The structure contains one-dimensional zigzag chains $^{1}_{\infty}|Ge^{2-}$ extending along the monoclinic axis and bent GeN_2^{4-} anions. Since the R-factor is so large, the Ge−N or Sr−N distances should be regarded with caution. The Ge−N distances we find are 1.84(3) and 1.94(2) Å, and the N−Ge−N angle is 104(1)°; bearing in mind the large uncertainties, these are similar to the equal distances of 1.883(7) and 1.873(9) Å and angle of 107.0(4)° in $Ba_3Ge_2N_2$. The Ge−Ge distance within the chains is 2.451(4) Å, which is identical to that in elemental Ge, and very similar to that in $Ba_3Ge_2N_2$ (2.50 Å). The crystallographic results are presented in Table 1, and the atomic parameters are given in Table 2. Anisotropic refinement of the displacement parameters of the heavy atoms indicated that they were approximately isotropic. Bond lengths and anisotropic thermal parameters are available as Supporting Information. The simulated powder diffraction pattern was very similar to the experimental pattern.

Crystal Structure of Sr_2GeN_2. The crystals of this material were well-formed rectangular prisms, and an analytical absorption correction based on the space group and unit cell contents was carried out. Data for a ψ-scan correction were also collected. The systematic extinctions suggested $P4_2/mbc$ and $P4_2bc$ as possible space groups. Structure solution using direct methods in $P4_2/mbc$ suggested an Sr:Ge ratio of 2:1, which is again at the high end of the range indicated by EDAX analysis. The N atoms were located during the initial stages of refinement and the Sr:Ge:N ratio was determined to be 2:1:2. The stoichiometry A_2GeN_2 (A = alkaline earth) has not previously been reported. Refinement of the structure was carried out in $P4_2/mbc$ using data corrected using the analytical absorption correction. The results are in Table 1. There was no indication that the symmetry is lower. If the shape of the crystal was kept constant but the size was allowed to vary, an R-factor of 3.5% was achieved when the dimensions were reduced by about three times the estimated error in the size measurement. This resulted in a negligible change in the structural parameters which are given in Table 3. Anisotropic refinement of the thermal displacement parameters of the N atoms indicated that they were approximately isotropic but did not improve the refinement and reduced the data to parameter ratio below 10. Anisotropic thermal displacement parameters for the heavy atoms are available as Supporting Information. When the structure was refined using the ψ-scan corrected data, the R-factor could only be reduced to 8.7%, indicating that the analytical correction is superior in this case. The simulated powder diffraction pattern matched the experimental pattern very closely indicating that there was very little contamination by impurity phases.

Table 3. Atomic Parameters for Sr_2GeN_2

atom	x	y	z	U_{eq}[a]
Sr(1)	0.3671(1)	0.4190(1)	0	10.0(7)
Sr(2)	0.0224(1)	0.3482(1)	0	9.6(7)
Ge(1)	0.2559(1)	0.1514(1)	0	10.1(7)
N(1)	0.0996(9)	0.1340(7)	0	10(2)
N(2)	0.3353(9)	0.0131(7)	0	9(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 $\mathbf{U}_{ij}$ tensor.

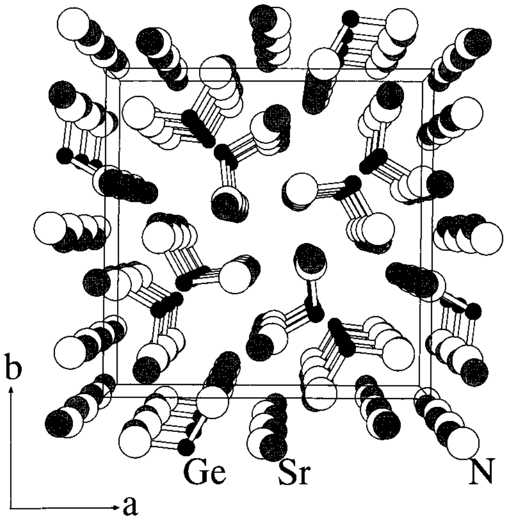

Figure 1. Structure of Sr_2GeN_2 viewed along the tetragonal axis. The Ge−N bonds and the unit cell are shown.

Table 4. Atomic Separations and Bond Angles in Sr_2GeN_2.

Sr(1)- -N(1)	2.562(9)	Sr(2)−N(2)	2.564(9)
Sr(1)−N(1)	2.713(1)[2][a]	Sr(2)−N(2)	2.741(2)[2]
Sr(1)−N(1)	2.807(11)	Sr(2)−N(2)	2.741(10)
Sr(1)−N(2)	2.628(10)	Sr(2)−N(1)	2.681(9)
Sr(1)−Ge(1)	3.095(2)	Sr(2)−Ge(1)	3.137(2)
Sr(1)−Ge(1)	3.406(1) [2]		
Ge(1)- -N(1)	1.851(11)	Ge(1)−N(2)	1.877(9)
N(1)−Ge(1)	1.851(11)	N(2)−Ge(1)	1.877(9)
N(1)−Sr(1)	2.562(9)	N(2)−Sr(2)	2.564(9)
N(1)−Sr(1)	2.713(1)[2]	N(2)−Sr(2)	2.741(2)[2]
N(1)−Sr(1)	2.807(11)	N(2)−Sr(2)	2.741(10)
N(1)−Sr(2)	2.681(9)	N(2)−Sr(1)	2.628(10)
N(1)−Ge(1)−N(2)	113.6(5)		

[a] The numbers in brackets indicate the number of bonds of a particular type.

The structure of Sr_2GeN_2 is shown in Figure 1, and bond lengths and angles are listed in Table 4. There are stacks of GeN_2^{4-} units extending along the c-axis. The Ge−N bond lengths are 1.85(1) and 1.88(1) Å, and the N−Ge−N bond angle is 113.6(5)°. This angle is somewhat larger than that in the similar units present in $Ba_3Ge_2N_2$[5] (107.0°). The two Ge−N bond lengths in $Ba_3Ge_2N_2$ are equal to one another within error. It is not clear whether the apparent slight difference in the two Ge−N bond lengths in Sr_2GeN_2 is real or due to the low scattering power of N compared to Sr or Ge; neutron diffraction using larger crystals would establish this with certainty. The GeN_2^{4-} units are isoelectronic with SO_2 and have 18 valence electrons. The bond angle in GeN_2^{4-} is intermediate between those in SO_2 (119.5°) and $SnCl_2$ (95°), which is consistent with VSEPR theory and molecular orbital considerations.

The Ge−Ge distance between adjacent GeN_2^{4-} units is 3.112(2) Å, and the Ge−Ge−Ge angle is 120.6(3)° This distance is considerably longer than Ge−Ge bond distances,

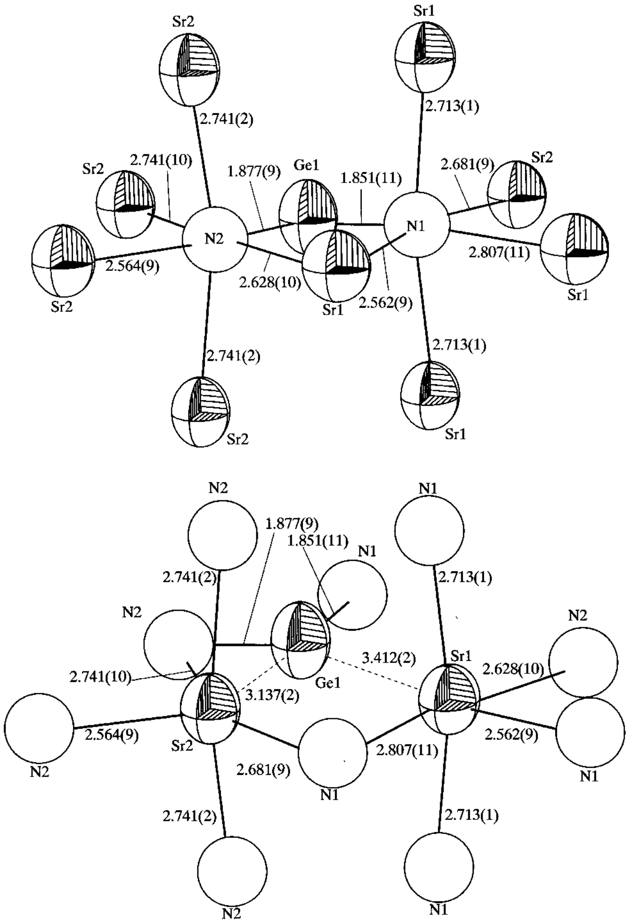

Figure 2. (a) Top: Coordinations of the N and Ge atoms in Sr_2GeN_2. (b) Bottom: Coordinations of the Sr atoms in Sr_2GeN_2. The Sr are 5-coordinate by N atoms located at 5 of the corners of distorted octahedra, and the sixth coordination site is directed toward the region occupied by the Ge lone pairs. The cation thermal ellipsoids are shown in this figure; since N was refined isotropically, it is shown as spheres. Bond distances are given in Å. The thermal ellipsoids are shown at the 99.9% probability level for clarity.

which are usually in the range 2.4−2.6 Å; however, it appears to be somewhat shorter than the distance one would expect for a van der Waals separation by analogy with, for example, Se. A distance of 3.095(2) Å is found for the Ge−Sr distance between opposite corners of the N−Ge−N−Sr quadrangle shown in Figure 2a. This relatively short distance is probably not due to a direct Ge−Sr interaction but rather due to the bonding of both these atoms to a common pair of N atoms. Other Ge−Sr distances of 3.137(2) Å for Ge−Sr2 and 3.412(2) Å for Ge−Sr1 shown in Figure 2b probably indicate weak coordination of the Sr by the Ge lone pairs, as described in $Ba_3Ge_2N_2$.[5] The atomic coordinations together with the thermal ellipsoids are shown in Figure 2. The coordination of N is 6, as it almost always is in nitrides.

Summary

We have synthesized two new strontium germanium nitrides from a Na flux and have determined that the structural motifs are very different from those in Ge_3N_4 or in germanium oxide chemistry in which Ge is tetrahedrally coordinated. The stoichiometry of the metals in the products is close to that of the reactants. This soft route seems to be a good way of stabilizing such non-metal nitrides and favors discrete units rather than extended structures. The nitride chemistry of Si is dominated by silicate-like structures containing infinitely linked SiN_4 units which are typically synthesized at very high temperatures (≥1500 °C).[16−19] However, when the low-temperature Na flux reactions are carried out with Ba and Si along with Na and NaN_3,[4] alkaline earth rich crystals, $Ba_5Si_2N_6$, are grown which contain small $Si_2N_6^{10-}$ units consisting of a pair of edge sharing SiN_4 tetrahedra. Ge-containing nitrides are unstable at very elevated temperatures; for example, Ge_3N_4 decomposes under 1 atm of NH_3 or N_2 to the elements at 850 °C, and so softer routes are necessary for the synthesis of these phases. Under these conditions, the range of Ge environments contrasts with what is known about silicon nitride chemistry and with germanium oxide chemistry. Thus the contrast between Si and Ge is much more marked in nitride chemistry than it is in oxide chemistry. Tetrahedral GeN_4 units are found in Ge_3N_4, the stuffed β-cristobalite $CaGeN_2$,[20] and the wurtzite $MgGeN_2$,[21] but with the heavier alkaline earths there seems to be more tendency for Ge to be formally divalent and to exhibit catenated motifs.

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Supporting Information Available: Text giving additional experimental information (4 pages). Two X-ray crystallographic files, in CIF format, are available. Access and ordering information is given on any current masthead page.

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