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New Calcium Germanium Nitrides: Ca_2GeN_2, Ca_4GeN_4, and $Ca_5Ge_2N_6$

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We report three new calcium germanium nitrides synthesized as crystals from the elements in sealed niobium tubes at 760 °C using liquid sodium as a growth medium. Black Ca_2GeN_2 is isostructural with the previously reported strontium analogue. It is tetragonal $P4_2/mbc$ (no. 135) with $a = 11.2004(8)$ Å, $c = 5.0482(6)$ Å, and $Z = 8$. It contains GeN_2^{4-} units which have 18 valence electrons, and consequently are bent, like the isoelectronic molecule SO_2. In contrast, clear, orange Ca_4GeN_4 with fully oxidized germanium contains isolated GeN_4^{8-} tetrahedra and is monoclinic $P2_1/c$ (no. 14) with $a = 9.2823(8)$ Å, $b = 6.0429(5)$ Å, $c = 11.1612(9)$ Å, $\beta = 116.498(6)°$, and $Z = 4$. Clear, colorless $Ca_5Ge_2N_6$, also with fully oxidized germanium, contains infinite chains, ${}^1_\infty[GeN_2N_{2/2}{}^{5-}]$, of corner-sharing tetrahedra similar to those found in pyroxenes. However, the precise structure of this latter phase has not yet been determined because of twinning problems.

Introduction

Interest in the chemistry of ternary nitrides has grown in recent years, partly as a result of the technological applications of many binary nitrides, and partly as a result of advances in synthetic methodology. In general, the synthesis of ternary nitrides is more synthetically demanding than that of the analogous oxides, sulfides, halides or phosphides as summarized elsewhere.[1] One convenient route for the synthesis of single crystals of ternary nitrides containing alkaline earths and late transition or main group metals is to grow them from a melt of sodium and the other metals held under a pressure of several atmospheres of N_2 in sealed metal tubes.[2−12] Sodium does not form a stable binary nitride, presumably because the coordination requirements of the sodium and nitride ions cannot both be simultaneously satisfied in material with stoichiometry Na_3N, and it is found empirically that sodium is only rarely[2] incorporated into the products of these reactions. Sodium appears to act as a growth medium or a flux for the growth of ternary nitrides in these reactions. Although nitrogen is insoluble in molten sodium, it does dissolve in these mixed metal melts as shown by the work of Simon and co-workers.[13−15]

We have been investigating ternary nitrides containing alkaline-earth metals and later main-group metals to assess the range of structures exhibited by these materials, and their relation to other classes of materials such as oxides, sulfides, and the higher pnictides. In the course of investigations in our group we have used the molten sodium technique to synthesize a range of new nitrides with a range of new structure types.[3−12] These materials contain a range of $M_xN_y^{n-}$ units (M = transition or main-group metal). $Ba_5Si_2N_6$,[3] Ba_2ZnN_2 and Sr_2ZnN_2,[4] Ba_3ZnN_2O,[5] $Sr_6Cu_3N_5$,[6] $Ba_3Ge_2N_2$,[7] and $Sr_3Ge_2N_2$ and Sr_2GeN_2[8] contain discrete nitridometalate anions: $Si_2N_6^{10-}$,[3] ZnN_2^{4-},[4,5] CuN_2^{5-} and $Cu_2N_3^{7-}$,[6] and GeN_2^{4-}.[7,8] One-dimensional chains, ${}^1_\infty[GaN_{4/2}{}^{3-}]$, of edge-sharing tetrahedra are found in $Ba_3Ga_2N_4$[9] and $Sr_3Ga_2N_4$,[10] while SrCuN[6] contains ${}^1_\infty[CuN_{2/2}{}^{2-}]$ chains. α-$Ca_3Ga_2N_4$[10] has a two-dimensional ${}^2_\infty[GaN_{4/2}{}^{3-}]$ anionic framework, while β-$Ca_3Ga_2N_4$[11] and $Sr_3Ga_3N_5$[10] have three-dimensional anionic frameworks. The compounds containing discrete nitridometalate anions are alkaline-earth-metal-rich and extremely sensitive to aerial hydrolysis. As the dimensionality of the anionic nitride framework increases, the materials become less alkaline-earth-metal-rich and the crystals of the three-dimensional framework materials are resistant to aerial hydrolysis for a few hours. Although these materials are synthesized under several atmospheres of nitrogen, the metals are frequently not found in their highest oxidation states: Cu(I) is the normal oxidation state of copper in nitrides, and Ge(II) is found as well as Ge(IV). This reflects the fact that nitrogen is less oxidizing than oxygen.

The only previously reported and characterized calcium germanium nitrides are $CaGeN_2$ with a stuffed β-cristobalite-type framework[16] and Ca_3GeN[17] with formally anionic germanium in the anti-perovskite-type structure. Here we report the synthesis of three new calcium germanium nitrides including Ca_4GeN_4, which contains the first example of an isolated GeN_4^{8-} unit analogous to the units in orthosilicates and orthogermanates, and $Ca_5Ge_2N_6$, which contains infinite chains

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$^1_\infty[GeN_2N_{2/2}^{5-}]$ of corner-linked GeN_4 tetrahedra similar to those found in the pyroxene silicates.

Experimental Section

Synthesis. All materials were handled in a 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%), Ca (Aldrich Chemical Co., 99+%), and Ge (Cerac 99.999%). Ge was obtained as chunks and ground to −300 mesh in the drybox to avoid oxide contamination. Ca_2GeN_2 and $Ca_5Ge_2N_6$ were prepared as crystals from the same reaction mixture (reaction 1), and it has not, so far, proved possible to synthesize either material exclusive of the other. For reaction 1 the following amounts of reactants were placed in the tube, NaN_3 (81 mg), Na (48 mg), Ca (20 mg), and Ge (25 mg), so that the molar ratio Na:Ca:Ge:N was about 10:1.5:1:11. Ca_4GeN_4 was prepared (reaction 2) along with some Ca_2GeN_2 from more Ca-rich melts, NaN_3 (83 mg), Na (50 mg), Ca (39 mg), and Ge (25 mg), so that the molar ratio Na:Ca:Ge:N was about 10:3:1:11. 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 in silica 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, whence the furnace was turned off. The tubes were cut open in the drybox 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 Ca, and then dried under vacuum.

Elemental Analysis. The approximate ratio of the heavy elements (Na or heavier) was determined using electron probe microanalysis (EPMA) using a JEOL 733 Superprobe instrument equipped with software for performing standardless quantitative analysis. This technique could not be used to determine the N content of the materials because the X-rays produced from N were absorbed by the Be window of the detector, and it was not possible to perform a windowless measurement using this instrument.

Crystal Structure Determination. All three materials are extremely air-sensitive, producing ammonia on contact with moist air. Hence, the crystals for X-ray diffraction were mounted using 5 min epoxy cement on thin glass fibers inside dry glass capillary tubes which were sealed inside 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 for Ca_2GeN_2, Ca_4GeN_4, and $Ca_5Ge_2N_6$ were determined using 37, 38, and 40 well-centered reflections, respectively, using a least-squares procedure. Data were collected using the Siemens XSCANS software.[18] 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.[19] Absorption corrections carried out using ψ scans were found to be satisfactory. 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 were carried out using the SHELXTL version5 suite.[20] An extinction correction was applied during the refinements.

Table 1. Crystallographic Data for Ca_2GeN_2 and Ca_4GeN_4

empirical formula	Ca_2GeN_2	Ca_4GeN_4
formula weight	180.77	288.94
space group	$P4_2/mbc$ (no. 135)	$P2_1/c$ (no. 14)
a, Å	11.2004(8)	9.2823(8)
b, Å		6.0429(5)
c, Å	5.0482(6)	11.1612(9)
β, deg		116.498(6)
vol, Å^3	633.3(1)	560.3(1)
Z	8	4
density (calcd), g cm^{-3}	3.792(1)	3.425(1)
temp, K	293	293
wavelength, Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
abs coeff, mm^{-1}	12.63	9.01
max, min transmission	0.28, 0.23	0.44, 0.36
R1[a]	0.0165	0.0302
wR2[b]	0.0362	0.0726

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^2)^2]^{1/2}$, where $w = 1/[\sigma(F_o^2)^2 + (gP)^2 + jP]$, $P = (\max(F_o^2,0) + 2F_c^2)/3$, $g = 0.011$ for Ca_2GeN_2 and 0.0361 for Ca_4GeN_4, and $j = 0.000$ for Ca_2GeN_2 and 0.2097 for Ca_4GeN_4.

Table 2. Atomic Parameters for Ca_2GeN_2[a]

atom	x	y	z	U_{eq}
Ca(1)	0.36719(9)	0.42420(9)	0	8.4(3)
Ca(2)	0.02108(9)	0.34983(9)	0	8.1(3)
Ge(1)	0.25469(5)	0.15590(4)	0	7.9(2)
N(1)	0.0899(4)	0.1362(4)	0	9.3(9)
N(2)	0.3358(4)	0.0097(3)	0	9.9(9)

[a] All atoms are on the 8h site. The equivalent isotropic thermal displacement parameter U_{eq} in Å^2 × 10^3 is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

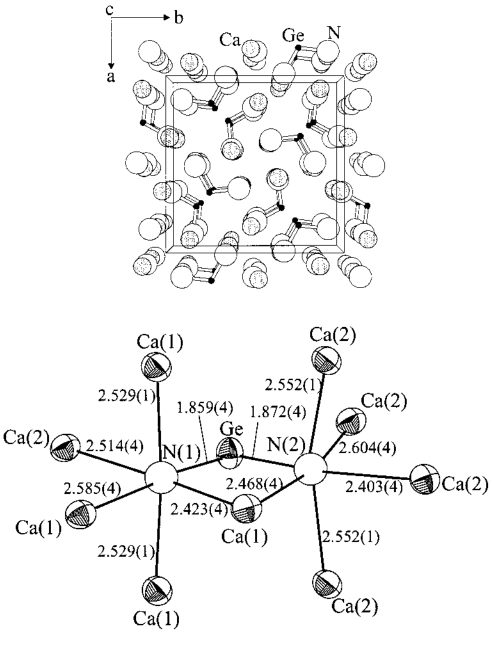

Figure 1. (a, top) Structure of Ca_2GeN_2 viewed down the tetragonal axis. (b, bottom) Coordinations of the N and Ge atoms in Ca_2GeN_2. The thermal ellipsoids are shown at the 99% level. N was refined isotropically, and is shown as spheres. Bond distances are given in angstroms.

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Table 3. Atomic Separations and Bond Angles in Ca_2GeN_2[a]

Ca(1)−N(1)	2.423(4)	Ca(2)−N(2)	2.403(4)
Ca(1)−N(1)	2.529(1) [2]	Ca(2)−N(2)	2.552(1) [2]
Ca(1)−N(1)	2.585(4)	Ca(2)−N(2)	2.604(4)
Ca(1)−N(2)	2.468(4)	Ca(2)−N(1)	2.514(5)
Ca(1)−Ge(1)	2.932(1)	Ca(2)−Ge(1)	2.985(1)
Ca(1)−Ge(1)	3.233(1) [2]	Ca(2)−Ge(1)	3.248(1) [2]
Ca(1)−Ge(1)	3.259(1)		
Ge(1)−N(1)	1.859(4)	Ge(1)−Ge(1)	2.894(1) [2]
Ge(1)−N(2)	1.872(4)		
N(1)−Ge(1)−N(2)	112.2(2)		

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

Results and Discussion

The products of both reactions appeared to be dark gray powders. When inspected using an optical microscope, it was clear that the product of reaction 1 contained both clear colorless lamellar needles which often occurred as aggregates ($Ca_5Ge_2N_6$) and, additionally, small black crystals which were almost cubic in shape (Ca_2GeN_2). EPMA on a few crystals of each type indicated that the Ca:Ge ratio in both cases was close to 2:1, quite similar to the ratio in the reaction mixture. The product of reaction 2 contained a large number of clear orange crystals (Ca_4GeN_4) which had a Ca:Ge ratio of about 4:1 by EPMA. No Na or other elements were detected in the EPMA experiment. These ratios were not consistent with the previously reported Ca−Ge−N phases.[16,17] Automatic indexing of the reflections measured using single-crystal diffraction confirmed that the three materials were new phases and suggested that the black material (Ca_2GeN_2) is isostructural with Sr_2GeN_2.[8] The crystallographic information for Ca_2GeN_2 and Ca_4GeN_4 is presented in Table 1.

Crystal Structure of Ca_2GeN_2. The absorption correction was carried out using a ψ scan with 37 reflections measured in 18 different orientations of the crystal. The systematic extinctions suggested $P4_2/mbc$ and $P4_2bc$ as possible space groups. Structure solution for the Ca and Ge using direct methods in $P4_2/mbc$, followed by location of the N atoms in the early stages of refinement, confirmed the material to be isostructural with Sr_2GeN_2.[8] Refinement of the structure was carried out in $P4_2/mbc$, and the results are given in Table 1. The final R factor (R1) was 1.65%. Anisotropic refinement of the thermal displacement parameters of the N atoms indicated that they were approximately isotropic, and thus their inclusion did not improve the refinement.

The structure of Ca_2GeN_2 is shown in Figure 1a. A fuller description of the structure is given in ref 8 (for Sr_2GeN_2). Atomic parameters are listed in Table 2, and bond lengths and angles are listed in Table 3. There are stacks of GeN_2^{4-} units extending along the c axis. The Ge−N bond lengths are 1.859(4) and 1.872(4) Å, and thus almost equal to each other and to the distances in Sr_2GeN_2 within error. The N−Ge−N bond angle is 112.2(2)°, very similar to that in Sr_2GeN_2 (113.7(5)°) and somewhat larger than that in the similar units present in $Ba_3Ge_2N_2$[7] (107.0°). Figure 1b shows the coordination about the N and Ge atoms and the thermal ellipsoids of all the atoms.

Crystal Structure of Ca_4GeN_4. 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 32 reflections were measured in 18 different orientations of the crystal. The systematic extinctions were consistent with the monoclinic space group $P2_1/n$ (a nonstandard setting of $P2_1/c$). Structure solution in $P2_1/n$ using direct methods located the Ca and Ge atoms, and the N atoms were located in the early stages of refinement. Refinement of the structure was carried out in $P2_1/c$ after conversion of the axes and atomic coordinates to the conventional setting using the SHELXTL software.[20] The results are in Table 1. The final R factor (R1) was 3.02%. All atoms were refined anisotropically.

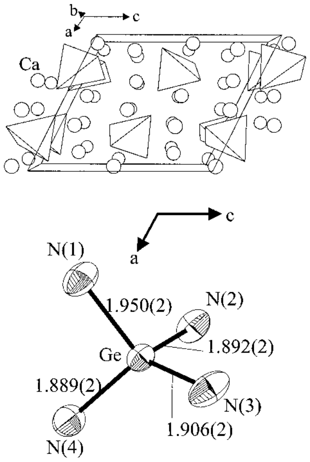

Figure 2. (a, top) Structure of Ca_4GeN_4 viewed down the monoclinic axis. (b, bottom) GeN_4 tetrahedron with thermal ellipsoids shown at the 99% level and bond distances given in angstroms.

Table 4. Atomic Parameters for Ca_4GeN_4[a]

atom	x	y	z	U_{eq}
Ca(1)	0.07798(6)	0.75612(9)	0.04371(6)	7.5(1)
Ca(2)	0.14675(7)	0.34522(9)	0.27039(6)	8.7(1)
Ca(3)	0.54803(7)	0.42246(9)	0.38031(6)	7.1(1)
Ca(4)	0.65326(7)	0.4167(1)	0.15562(6)	9.9(1)
Ge(1)	0.26924(3)	0.35885(5)	0.05185(3)	5.4(1)
N(1)	0.0959(3)	0.0186(4)	0.3902(2)	8.6(4)
N(2)	0.1976(3)	0.1117(4)	0.1146(2)	7.7(5)
N(3)	0.3368(3)	0.5841(4)	0.1854(3)	9.3(5)
N(4)	0.4111(3)	0.2468(4)	0.4852(2)	8.0(4)

[a] All atoms are on the 4e site. The equivalent isotropic thermal displacement parameter U_{eq} in $Å^2 \times 10^3$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The structure of Ca_4GeN_4 is shown in Figure 2a, atomic parameters are listed in Table 4, and bond lengths and angles are listed in Table 5. The structure consists of slightly distorted GeN_4 tetrahedra isolated from one another. The N atoms are all six-coordinate, as is commonly found in nitride chemistry. The Ca atoms are all five-coordinate. Figure 2b shows the coordination about the Ge atom. The structure is not closely related to those of the known alkali-metal orthosilicates, orthogermanates, orthostannates, orthoplumbates, or orthotitanates with similar stoichiometries. In the structures adopted by such compounds containing the smaller alkali-metal cations (Li−K), one or more of the alkali-metal ions are always four-coordinate by oxygen, meaning that one or more oxide ions are five-coordinate by the metal ions. In the Rb and Cs compounds, one of the cations is six-coordinate by oxygen. Among the isostoichiometric orthothiosilicates, orthothiogermanates, orthothiostannates, orthothioplumbates, and orthothiotitanates, only Na_4SnS_4[21] has coordination *numbers* for all atoms which are similar to those in Ca_4GeN_4, but the structure of Na_4SnS_4 is of much higher symmetry, and there is no close relationship between this structure and that of Ca_4GeN_4. The known higher pnictide analogues of Ca_4GeN_4: A_4ME_4 (A = Sr, Ba; M = Si,

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Table 5. Atomic Separations and Bond Angles in Ca$_4$GeN$_4$

Ca(1)−N(1)	2.444(2)	Ca(2)−N(1)	2.405(2)	N(4)−Ge(1)−N(2)	107.5(1)
Ca(1)−N(1)	2.504(3)	Ca(2)−N(1)	2.544(3)	N(4)−Ge(1)−N(3)	120.4(1)
Ca(1)−N(2)	2.386(3)	Ca(2)−N(2)	2.444(3)	N(4)−Ge(1)−N(1)	101.3(1)
Ca(1)−N(2)	2.504(2)	Ca(2)−N(3)	2.755(3)	N(2)−Ge(1)−N(3)	108.8(1)
Ca(1)−N(3)	2.442(3)	Ca(2)−N(4)	2.621(2)	N(2)−Ge(1)−N(1)	111.2(1)
				N(3)−Ge(1)−N(1)	107.5(1)
Ca(3)−N(4)	2.332(2)	Ca(4)−N(4)	2.415(2)		
Ca(3)−N(3)	2.393(3)	Ca(4)−N(4)	2.443(2)		
Ca(3)−N(4)	2.426(3)	Ca(4)−N(2)	2.591(2)		
Ca(3)−N(3)	2.561(3)	Ca(4)−N(3)	2.656(3)		
Ca(3)−N(2)	2.601(3)	Ca(4)−N(1)	2.669(3)		
Ge(1)−N(4)	1.889(2)	Ge(1)−N(3)	1.906(2)		
Ge(1)−N(2)	1.892(2)	Ge(1)−N(1)	1.950(2)		

Ge; E = P, As), have the Ba$_4$SiP$_4$ structure [22] with isolated ME$_4$ tetrahedra, but in which the pnictide anion is seven-coordinate and the alkaline-earth metal is six-coordinate. The structure of Ca$_4$GeN$_4$ is likely determined by the preference of the nitride anion for a six-coordinate site.

Crystal Structure of Ca$_5$Ge$_2$N$_6$. It was not possible to index the faces of the crystal due to its irregular shape, so the absorption correction was carried out using ψ scans in which 39 reflections were measured in 18 different orientations of the crystal.

Several unusual systematic extinction conditions were apparent, suggesting probable twinning, and these were consistent for all the crystals of this composition measured. A number of primitive orthorhombic space groups were consistent with the absences, but monoclinic symmetry in $P2_1/c$ could not be ruled out. Direct methods were used in $P2_1/c$ to obtain the starting structural model for the Ca and Ge atoms. The structure could then be refined in the orthorhombic space group *Pbca* (no. 61) with $a = 5.2342(6)$ Å, $b = 21.561$ Å, $c = 13.125$ Å, and $Z = 8$. The nitrogen atoms were located during the initial stages of least-squares refinement. This analysis indicated that the true Ca:Ge:N ratio was 5:2:6. Refinement in *Pbca* produced a final R1 of 3.1% for $F_o > 4\sigma$ and a wR2 of 7.5% for all data. However, this model was unsatisfactory because pairs of atoms were related by an additional symmetry operation, $^1/_2 - x$, $^1/_4 - y$, $^1/_2 - z$, which suggests that halving of the b axis is necessary, together with twinning to explain the high intensity of the hkl reflections with $k = 2n + 1$.

The single-crystal studies clearly indicate that Ca$_5$Ge$_2$N$_6$ contains infinite chains $^1_\infty$[GeN$_2$N$_{2/2}{}^{5-}$] of corner-linked GeN$_4$ tetrahedra. These chains are similar to those found in the orthorhombic and monoclinic pyroxenes ortho-[23] and clinoenstatite[24] (both MgSiO$_3$); however, we are unable to determine exactly how the chains are arranged with respect to one another in the unit cell. It should be noted that, like Ca$_5$Ge$_2$N$_6$, orthoenstatite appears to crystallize in orthorhombic *Pbca*, but there is evidence that this compound is actually monoclinic and twinned by a glide operation.[23−25] Such twinning has also been described by Dunitz;[26] however, we have not yet been able to elucidate the twin law for Ca$_5$Ge$_2$N$_6$. The structure is completely different from those of the isostoichiometric compounds Ba$_5$Si$_2$N$_6$[3] and Sr$_5$Ge$_2$N$_6$[12] which contain isolated units, M$_2$N$_6{}^{10-}$ (M = Si, Ge), composed of a pair of edge-sharing MN$_4$ tetrahedra. Infinite chains of tetrahedra with similar connectivities have been reported in several alkali-metal/early-transition-metal nitrides[27] and in the isostoichiometric phosphide Sr$_5$Sn$_2$P$_6$,[28] but in all these cases the chain geometry is completely different from that in Ca$_5$Ge$_2$N$_6$ and the pyroxene oxides.

Summary

We have synthesized three new calcium germanium nitrides from molten sodium and have determined that very different structural motifs and oxidation states are attainable in ternary germanium nitrides, and further that these may be present in different materials grown from the same reaction. Ca$_4$GeN$_4$ is a nitride analogue of the orthosilicates and orthogermanates, albeit with no direct structural relative in those classes of compounds. Despite its different stoichiometry, Ca$_5$Ge$_2$N$_6$ can be thought of as the first nitride analogue of the pyroxene class of silicates. Ca$_2$GeN$_2$, on the other hand, contains structural motifs which have not been found in the corresponding oxide chemistry, but which appear to be characteristic of nitride chemistry. Whether all these materials form under similar conditions during the reaction is uncertain, and has not yet been investigated.

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Supporting Information Available: Two X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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