

The synthesis and structural characterization of the new ternary nitrides: Ca_4TiN_4 and Ca_5NbN_5

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Abstract

The ternary nitrides, Ca_4TiN_4 and Ca_5NbN_5 , were synthesized in sealed niobium tubes using lithium nitride as a flux at 900 and 1050 °C, respectively. The structures of both compounds were solved from single-crystal X-ray diffraction data. Ca_4TiN_4 is the first example of a calcium group IV nitride; it crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with cell parameters $a = 5.9757(5)$ Å, $b = 6.0129(5)$ Å, $c = 6.0116(12)$ Å, $\alpha = 71.565(4)^\circ$, $\beta = 79.471(4)^\circ$, $\gamma = 68.258(4)^\circ$ and $Z = 2$. Ca_4TiN_4 is isostructural with Na_4TiO_4 and contains tetrahedral TiN_4 units connected through edges and corners to CaN_4 tetrahedra and CaN_5 square pyramids. Ca_5NbN_5 crystallizes in the monoclinic space group $C2/m$ (No. 12) with cell parameters $a = 11.922(7)$ Å, $b = 6.878(5)$ Å, $c = 8.936(7)$ Å, $\beta = 101.22(3)^\circ$ and $Z = 4$. Ca_5NbN_5 is isostructural with Ba_5NbN_5 ; the structure contains NbN_4 tetrahedra that share vertices with CaN_5 trigonal bipyramids.

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1. Introduction

Nitride compounds of the group IV elements, titanium, zirconium and hafnium, which also include an alkali metal or alkaline earth element are relatively few in number. The only ternary lithium titanium nitride is Li_5TiN_3 [1], and the two known alkaline earth ternary titanium nitrides are $\text{Ba}_{10}\text{Ti}_4\text{N}_{12}$ [2] and SrTiN_2 [3]. Until now, there have been no known nitrides containing both calcium and a group IV element. This lack prompted the exploration of this section of the periodic table. Many syntheses were attempted using lithium nitride as a flux, with calcium or calcium nitride (Ca_3N_2 or Ca_2N), and the group IV metal or metal nitride. One of them was particularly successful and resulted in a

new compound, Ca_4TiN_4 , the first example of a calcium group IV nitride.

In the chemical literature, there are seven nitride compounds that contain niobium and an alkaline earth element, and there are additional four compounds that also contain oxygen. Only one of these eight nitrides includes calcium as the alkaline earth element, CaNbN_2 [4,5], and this compound is also the most interesting. CaNbN_2 has been reported to exhibit a superconducting transition at approximately 14 K. The structure is layered, consisting of a series of NbN_2 layers stacked along the c direction and separated by hexagonal layers of Ca^{2+} cations. The niobium atoms are coordinated octahedrally and the calcium atoms are in the octahedral sites between the nitrogen sublayers of two different NbN_2 layers. Assigning the typical oxidation states of +2 and –3 to calcium and nitrogen, respectively, results in a d^1 formal electron count for niobium. CaNbN_2 is isostructural with CaTaN_2 [6], is apparently metallic and is also related to the layered LiMoN_2 [7] structure where molybdenum is not coordinated octahedrally by nitrogen but in a trigonal prismatic coordination.

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The initial goal of the experiments described in this paper was to synthesize Ca_3NbN_3 , which was thought to be possible based on the existence of Ca_3VN_3 [8]. That compound has an interesting transition metal environment with vanadium coordinated to nitrogen in a trigonal planar environment. The synthesis of Ca_3NbN_3 was not achieved; however, Ca_5NbN_5 was discovered and its synthesis and structural characterization is discussed.

2. Experimental

2.1. Synthesis of starting materials

All manipulations were carried out inside an argon-filled dry box. The starting materials, lithium nitride and calcium nitride were synthesized by the procedures listed below. Purchased lithium nitride appears to contain a small amount of hydrogen, and purchased calcium nitride contains oxygen impurities. Lithium nitride, Li_3N , was prepared using a slight alteration of procedures developed by Gregory et al [9]. Approximately 500 mg of elemental lithium (Aldrich ingot, 99.9%) was placed under approximately 800 mg of elemental sodium (Aldrich, A.C.S. reagent grade, distilled) in a stainless-steel crucible. The crucible was put into a molybdenum foil-lined stainless-steel reaction tube (1" diameter, 22" long) and reacted under flowing, purified nitrogen gas for 36 h at 650 °C. (Nitrogen gas was purified using a molecular sieve moisture trap, an Oxiclear gas purifier (oxygen filter) and a titanium wire (Aldrich, 0.81 mm diameter, 99.7%) ball as a getter placed just in front of the crucible). The sodium evaporated during heating, leaving only pure lithium nitride (purplish-black color) with an average yield of 95% remaining in the crucible. To prepare pure calcium nitride, Ca_3N_2 , the oxide coating of a piece of calcium rod (ESPI, 99.9%) was completely removed by filing. A 2" length of the cleaned calcium was placed in an alumina crucible inside a molybdenum foil-lined stainless-steel reaction tube. A second alumina crucible with sacrificial calcium was placed in front of the calcium rod crucible and the reaction tube was heated under flowing nitrogen gas purified as described above for 48 h at 1000 °C. The synthesized calcium nitride (average yield equaled 98%), a deep reddish-brown color, was then crushed in a stainless-steel compression mortar in the glove box before use.

2.2. Synthesis of Ca_4TiN_4

Ca_4TiN_4 was synthesized in a niobium tube which had previously been cleaned with a solution of 45% sulfuric acid, 40% nitric acid and 15% hydrofluoric acid to remove any surface oxidation. The starting materials, 401 mg (11.5 mmol) Li_3N , 608 mg (4.1 mmol) Ca_3N_2 , and 124 mg (2.0 mmol) TiN (Alfa Aesar, 99.5%) were loaded into a 1/4" pellet press. The pellet press was placed in a plastic bag with a small volume of argon and removed temporarily from the glove box while pressing a pellet under 1900 psi

pressure. The press was then immediately returned to the glove box. The pellet was removed from the press and placed into a 3"-long niobium tube, one end of which was previously welded closed in an arc furnace. The tube was subsequently sealed under an argon atmosphere in the arc furnace, sealed under vacuum into a silica tube, then heated to 900 °C over a 30-h period, held at 900 °C for 200 h, and cooled slowly over a period of 200 h.

2.3. Synthesis of Ca_5NbN_5

Ca_5NbN_5 was synthesized by loading 471 mg (13.5 mmol) Li_3N , 712 mg (4.8 mmol) Ca_3N_2 , and 186 mg (2.0 mmol) NbN (Alfa Aesar, 99%) into a 2"-long Nb tube. As before, the tube was sealed in an arc furnace under an argon atmosphere. The tube was then sealed under vacuum into a silica tube, heated to 1050 °C over a 30-h period, held at 1050 °C for 200 h and cooled slowly to room temperature over a period of 200 h.

2.4. Electron microprobe analysis

The elemental composition of the crystals was determined by electron microprobe analysis using a JEOL 8900 electron microprobe. Because of the air-sensitivity of the crystals, an air-sensitive sample holder was used. This device enables crystals to be transferred directly from the argon-filled glove box to the microprobe without air exposure and prevents oxygen contamination and possible decomposition of the crystals [10]. The heavier elements could be identified by electron microprobe EDS, but the lighter elements, lithium and nitrogen, could not be conclusively identified by this method due to their insufficient atomic weights. Wavelength dispersive microprobe (WDS) analysis was performed on the crystals to confirm the presence of nitrogen and identify any oxygen present. A small oxygen signal (less than 5% of the nitrogen signal) is typical during these measurements due to slight surface oxidation. Nitride compounds are often air-sensitive and it is very difficult to completely exclude air during transfer of the crystals. A slight oxygen signal generally does not indicate oxygen incorporation into the crystal structure whereas a larger oxygen signal may reflect the presence of oxygen within the crystal.

2.5. Single crystal X-ray analysis

A Bruker SMART system [11], equipped with a graphite monochromator, using $\text{MoK}\alpha$ radiation with a CCD detector was used to collect single-crystal diffraction data on the Ca_5NbN_5 crystals. The full data collection was done using exposure times of 30 s/frame. SAINT [11] software was used to integrate the data, and empirical absorption corrections were determined and applied using the SADABS [12] program. Crystals were mounted on a thin plastic loop using polybutene oil and cooled immediately to 165 K using a stream of cold nitrogen gas (which also held

the crystal stationary). A Bruker Apex II system [13] was used to collect single-crystal diffraction data on the Ca_4TiN_4 crystals. This new system is also equipped with a graphite monochromator and uses $\text{MoK}\alpha$ radiation with a CCD detector. After data collection, the systematic absences presented the possible space groups from which the crystal structure was solved using the SHELX software suite [14] with direct methods. An initial solution with the positions of some or all of the heavier atoms was found using SHELXS. Repeated least-squares refinement using SHELXL with Fourier difference maps determined the positions of any additional heavy atoms as well as the lighter atoms, nitrogen and lithium. The program AD-DSYM [15] was then used to confirm the choice of space group and STRUCTURE TIDY [16] software was used to standardize the atomic coordinates.

2.6. Eutax analysis

The Madelung site potentials and bond valence sums of the atoms in Ca_5NbN_5 were calculated with the software program EUTAX [17]. The internal value of the atomic bond distances were used in all cases. Only cation–anion interactions were used to calculate the bond valence sums and the Madelung site potentials were calculated assuming that the formal charges of the possible cations were their fully oxidized state: Li^+ , Ca^{2+} , Nb^{5+} , and that the formal charges of the possible anions were the usual: N^{3-} , O^{2-} .

The Madelung site potentials are calculated by replacing ions within a crystal with point charges equivalent to the formal charge of the ions. Thus, they are most useful for modeling ionic compounds such as oxides. However, even though the bonding in nitrides is often considerably more covalent than in oxides, it has been discovered that the Madelung site potentials calculated by Eutax are also useful for assigning atomic sites in nitrides [18]. Typically, the calculated site potentials in nitrides are approximately equal to -10 V multiplied by the formal charge of the ion.

The calculated bond valence sum of an atom would equal its valency in a completely ionic compound. Although no compound is purely ionic, and nitrides have a considerable amount of covalent bonding, the bond valence sum can still give an indication of the oxidation state of an atom in a particular site.

3. Results and discussion

3.1. Ca_4TiN_4

Upon opening the reaction tube in an argon-filled glove box, several chunks of silvery lithium with numerous small orange (LiCaN) and yellowish-orange crystals were found. The elemental composition of several of the yellowish-orange crystals was determined by electron microprobe analysis. The crystals observed had many nice crystal faces. Fifteen separate locations on three different crystals were tested by EDS and all locations contained both calcium

and titanium. A semi-quantitative analysis revealed the atomic ratio for $\text{Ca}:\text{Ti}$ to be 78.5:21.5. This ratio was the same within $\pm 1.5\%$ for the multiple positions examined on all three crystals. WDX analysis was performed on one crystal and showed a moderate nitrogen signal and only a very small oxygen signal ($<4\%$ of the nitrogen signal).

Crystals of Ca_4TiN_4 suitable for single-crystal diffraction experiments were selected from some of the many embedded in the matrix of lithium metal. The small, well-formed crystals were yellowish-orange in color, plate-shaped and air-sensitive. A crystal of approximate dimensions of $0.08 \times 0.08 \times 0.04\text{ mm}^3$ was selected. Initially, the cell parameters were determined using 93 well-centered reflections. After data collection, the systematic absences presented the possible space groups as $P1$ (chiral) and $P\bar{1}$ (centrosymmetric) with initial R values for these triclinic groups at $R_{\text{int}} = 0.029$. No other crystal system had a R_{int} value < 0.539 . The E -statistics function of the SHELX software suite indicated a strong probability of centrosymmetry at 85.3%. The crystal structure was solved in both space groups using direct methods with an initial solution containing the positions of the titanium atom and two of the calcium atoms. Repeated least-squares refinement determined the positions of two additional calcium atoms and four nitrogen atoms. Anisotropic refinement was successfully applied to all atoms. The higher symmetry space group choice, $P\bar{1}$, was confirmed and the crystallographic results are summarized in Table 1. The atomic coordinates were standardized with STRUCTURE TIDY [16] and are shown in Table 2. The anisotropic displacement parameters are shown in Table 3.

The R indices for the crystal structure determined are very good, $R_1 = 0.0147$, $wR_2 = 0.0392$ for $I > 2\sigma(I)$ and $R_1 = 0.0164$, $wR_2 = 0.0398$ for all data, and the remaining largest difference peak and deepest difference hole are very small, $+0.425$ and $-0.600\text{ e}^- \text{ \AA}^{-3}$, respectively, suggesting that all atom positions are accounted for.

The crystal structure of Ca_4TiN_4 is shown in Fig. 1. Ca_4TiN_4 is isostructural with Na_4TiO_4 [19], Na_4SiO_4 [20], and K_4SnO_4 [21] as well as several other oxides with the formula $A_4\text{MO}_4$ (A = alkali metal, M = transition group or main group element). All positions in the crystal structure are fully occupied. The structure contains an isolated tetrahedral position for the transition metal element, titanium. Four nitrogen atoms surround titanium in approximately tetrahedral geometry with bond lengths ranging from 1.941–1.970 Å, and bond angles from 102.57–118.38°. For comparison, the average Ti–N bond distance for tetrahedrally coordinated titanium in $\text{Ba}_{10}\text{Ti}_4\text{N}_{12}$ [2] is 1.951 Å. Titanium is bound to four crystallographically different nitrogen atoms and through each of these the TiN_4 tetrahedron shares vertexes with one or more calcium polyhedra. The TiN_4 tetrahedron also shares edges with four calcium polyhedra; three of these are shown in Fig. 2. The triclinic structure of Ca_4TiN_4 is quite complicated as evidenced by the irregular connection between the TiN_4 tetrahedron and the surrounding

Table 1
Crystal data and structure refinement for Ca₄TiN₄ and Ca₅NbN₅

Empirical formula	Ca ₄ TiN ₄	Ca ₅ NbN ₅
Formula weight	264.26	363.36
Temperature (K)	165	165
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>C</i> 2/ <i>m</i> (No. 12)
<i>a</i> (Å)	5.9757(5)	11.922(7)
<i>b</i> (Å)	6.0129(5)	6.878(5)
<i>c</i> (Å)	8.9881(7)	8.936(7)
α (deg.)	71.565(4)	90
β (deg.)	79.471(4)	101.22(3)
γ (deg.)	68.258(4)	90
Volume (Å ³)	283.80(4)	718.7(9)
<i>Z</i>	2	4
Density (calculated, Mg m ⁻³)	3.092	0.840
Absorption coefficient (mm ⁻¹)	5.002	1.291
<i>F</i> (000)	260	176
Crystal size (mm ³)	0.08 × 0.08 × 0.04	0.05 × 0.04 × 0.03
θ range for data collection (deg.)	2.40 to 33.14	2.32 to 30.50
Limiting indices	$-9 \leq h \leq 9, -9 \leq k \leq 9, -13 \leq l \leq 13$	$-16 \leq h \leq 16, -9 \leq k \leq 9, -12 \leq l \leq 12$
Reflections collected/unique	10196/2123 [<i>R</i> _{int} = 0.0290]	4047/1171 [<i>R</i> _{int} = 0.0308]
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2123/0/83	1171/0/65
Goodness-of-fit on <i>F</i> ²	1.088	1.069
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0147, <i>wR</i> ₂ = 0.0392	<i>R</i> ₁ = 0.0238, <i>wR</i> ₂ = 0.0609
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0164, <i>wR</i> ₂ = 0.0398	<i>R</i> ₁ = 0.0250, <i>wR</i> ₂ = 0.0614
Largest diff. peak and hole (e ⁻ Å ⁻³)	0.425 and -0.600	1.386 and -0.811

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^2)]^{1/2}}{F_c}$$

Table 2
Atomic coordinates for Ca₄TiN₄

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} Å ² × 10 ³
Ti(1)	2i	0.2839(1)	0.1523(1)	0.2443(1)	3(1)
Ca(1)	2i	0.2249(1)	0.4216(1)	0.8236(1)	6(1)
Ca(2)	2i	0.2642(1)	0.7722(1)	0.0189(1)	6(1)
Ca(3)	2i	0.2705(1)	0.5205(1)	0.4263(1)	5(1)
Ca(4)	2i	0.7648(1)	0.0458(1)	0.3924(1)	5(1)
N(1)	2i	0.0294(2)	0.2908(2)	0.3911(1)	5(1)
N(2)	2i	0.1155(2)	0.1685(2)	0.0737(1)	7(1)
N(3)	2i	0.4814(2)	0.3669(2)	0.1960(1)	6(1)
N(4)	2i	0.5114(2)	0.1760(2)	0.6376(1)	6(1)

Table 3
Anisotropic displacement parameters (Å² × 10³) for Ca₄TiN₄

Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Ti(1)	3(1)	4(1)	4(1)	-1(1)	0(1)	-1(1)
Ca(1)	6(1)	6(1)	6(1)	0(1)	-1(1)	-3(1)
Ca(2)	5(1)	5(1)	5(1)	-2(1)	-1(1)	-1(1)
Ca(3)	4(1)	5(1)	5(1)	-2(1)	0(1)	-2(1)
Ca(4)	5(1)	5(1)	6(1)	-1(1)	-1(1)	-2(1)
N(1)	5(1)	6(1)	6(1)	-2(1)	0(1)	-2(1)
N(2)	7(1)	7(1)	7(1)	-2(1)	-2(1)	-3(1)
N(3)	6(1)	6(1)	6(1)	-2(1)	0(1)	-2(1)
N(4)	6(1)	7(1)	7(1)	-1(1)	-1(1)	-2(1)

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

polyhedra. Another way to describe the structure is as layers of calcium and titanium atoms (in a 4:1 ratio) separated by layers of nitrogen atoms. The closest cation–cation contact in the Ca₄TiN₄ structure is Ca(2)–Ti at 3.101 Å. The Ca–Ti contacts range from 3.101–3.605 Å; the Ca–Ca contacts range from 3.156–3.525 Å. The structure of Ca₄TiN₄ can also be described as a distorted close-packed structure with nitrogen in the octahedral holes. There are five cations (four calcium, one titanium) for every four nitrogen anions, so 80% of the octahedral holes are filled, 20% are empty. Fig. 3 shows a space-filling model of the structure with every fifth octahedral hole empty.

Four crystallographically different calcium positions are present in Ca₄TiN₄. Three calcium positions are five-coordinate with two of these in a square-pyramidal geometry and the other in a distorted trigonal bipyramidal geometry. The fourth calcium is four-coordinate in a distorted tetrahedral environment. The Ca–N bond lengths for the four crystallographically different calcium atoms range from 2.392–2.847 Å (see Table 4).

The typical coordination number for nitrogen in nitride compounds is six. In Ca₄TiN₄, the four different nitrogen positions have coordination environments of five and six. Three nitrogen positions [N(1), N(3), N(4)] have fairly regular octahedra with one short bond: the Ti–N bond. The fourth nitrogen atom [N(2)] has a five-coordinate environment in a distorted square pyramid if the long Ca–N length of 2.848 Å is included. The average Ca–N

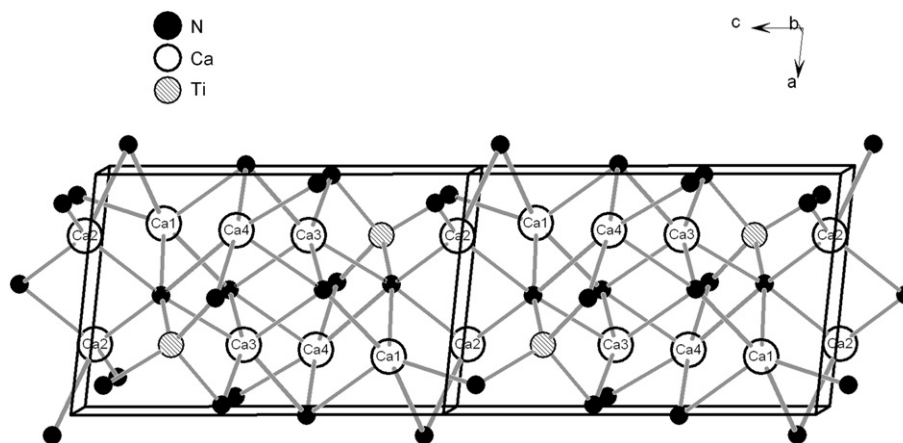


Fig. 1. Crystal structure of Ca_4TiN_4 along the $[0\ 1\ 0]$ direction showing two unit cells with layers of calcium and titanium atoms separated by layers of nitrogen atoms. Calcium atoms are shown as open circles, titanium atoms are hatched, and nitrogen atoms are in black.

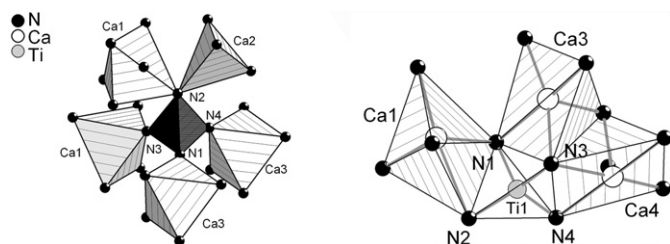


Fig. 2. Ca_4TiN_4 : titanium tetrahedra corner sharing with calcium polyhedra on the left, and edge sharing with calcium polyhedra on the right.

bond length of octahedrally coordinated nitrogen atoms is 2.487 \AA while the average bond distance for the five-coordinate nitrogen is 2.519 \AA .

Ca_4TiN_4 crystallizes in the $P\bar{1}$ space group with two formula units, $Z = 2$, and shares the same structure type with Na_4TiO_4 [19]. Both of these compounds have titanium in the +4 oxidation state. Assigning the typical oxidation states of +2 and -3 to calcium and nitrogen, and +1 and -2 to sodium and oxygen, respectively, it is perhaps expected that these two compounds adopt the same structure. The higher positive charge of the alkaline earth metal is offset by the higher negative charge of nitrogen; the structure has four atoms of each resulting in a charge of -4: $4(-3) + 4(+2) = -4$, which balances the +4 charge of titanium. In the same manner, the charges on sodium and oxygen also result in a charge of -4: $4(-2) + 4(+1) = -4$.

Ca_4TiN_4 is the only nitride with the Na_4TiO_4 structure type, but there are ten other oxides with transition metal or main group elements in the +4 oxidation state that share this same structure. A subset of nitrides and oxides includes those which, like Ca_4TiN_4 , have stoichiometries of one for the transition metal or main group cation, then equal subscripts for the alkali or alkaline earth element and anion. Even in this small subset, there are many nitrides besides Ca_4TiN_4 that crystallize in the same structure type as an oxide. For example, Ca_2ZnN_2 [22], Sr_2ZnN_2 [23],

Ba_2ZnN_2 [23] and Sr_2NiN_2 [24] are isotypic compounds that share the K_2NiO_2 [25] structure type.

The bond valence sums in Ca_4TiN_4 were analyzed using Eutax [17]. The values for the four calcium positions are 1.773, 1.835, 1.878 and 2.089; the value for the titanium position is 3.763. In addition, the values for the four nitrogen positions are 2.588, 2.609, 3.026 and 3.116. As is typical with nitrides, the numbers are not exact, rather they are useful in comparing one element to another, as is true here with calcium vs. titanium.

3.2. Ca_5NbN_5

The niobium reaction tube was opened in an Ar-filled glove box and dark-colored crystals were found adhering to the inner walls of the tube. Upon initial examination in an optical microscope these crystals appeared to be black in color, but after dividing some into smaller pieces they were observed to be dark orange in color. The elemental composition of two of the dark orange crystals was determined by electron microprobe. Ten locations from the flat faces of these crystals were tested; both crystals contained calcium and niobium. A semi-quantitative analysis of the composition revealed the atomic ratio for Ca:Nb to be 83:17. This ratio was consistent within $\pm 3\%$ for the multiple positions on both crystals. Wavelength dispersive (WDS) analysis indicated the presence of nitrogen and a minimal presence of oxygen (the oxygen signal was approximately 5% of the nitrogen signal).

Crystals of Ca_5NbN_5 suitable for single-crystal diffraction experiments were selected from the matrix of lithium metal. The crystals were dark orange and slightly air-sensitive. Many large blocks ($0.10 \times 0.08 \times 0.06\text{ mm}^3$) were present but none of these were determined to be single crystals. Several larger crystals were carefully trimmed using a small scalpel, and a crystal of approximate dimensions of $0.05 \times 0.04 \times 0.03\text{ mm}^3$ was selected. A Bruker SMART system was used to collect single-crystal diffraction data. Initially, the cell parameters were

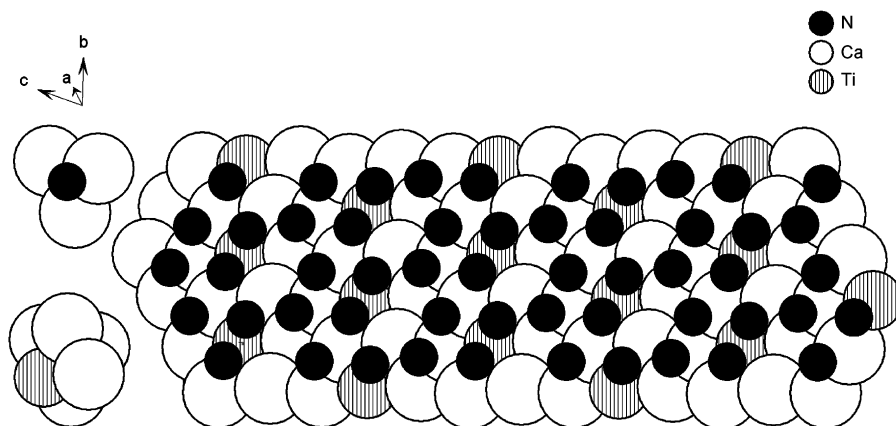


Fig. 3. View approximately along the [100] direction showing a space-filling model of Ca_4TiN_4 with a layer of calcium and titanium atoms with nitrogen atoms in the octahedral holes. 20% of the octahedral holes are empty corresponding to the 4:5 anion:cation ratio of the structure. The two sets of atoms on the left represent a single nitrogen atom in its octahedral hole with one layer showing (top) and the same nitrogen atom hidden beneath the top layer (bottom). Calcium atoms are shown as open circles, titanium atoms are hatched, and nitrogen atoms are black.

Table 4
Selected interatomic distances (\AA) for Ca_4TiN_4

Ti(1)–N(1)	1.9414(9)	Ti(1)–Ca(4)	3.1008(4)
Ti(1)–N(2)	1.9418(9)	Ti(1)–Ca(3)	3.1135(3)
Ti(1)–N(3)	1.9575(9)	Ti(1)–Ca(4)	3.1519(4)
Ti(1)–N(4)	1.9699(9)	Ti(1)–Ca(1)	3.1776(4)
Ca(1)–N(2)	2.4148(9)	Ti(1)–Ca(2)	3.3149(4)
Ca(1)–N(1)	2.4571(9)	Ti(1)–Ca(4)	3.3511(4)
Ca(1)–N(3)	2.4760(9)	Ti(1)–Ca(2)	3.5437(4)
Ca(1)–N(4)	2.5593(10)	Ti(1)–Ca(2)	3.6052(4)
Ca(1)–N(2)	2.8469(10)	Ca(1)–Ti(1)	3.1776(4)
Ca(2)–N(2)	2.3923(10)	Ca(1)–Ca(4)	3.1942(4)
Ca(2)–N(3)	2.3973(9)	Ca(1)–Ca(2)	3.2311(4)
Ca(2)–N(2)	2.4232(10)	Ca(1)–Ca(2)	3.2533(4)
Ca(2)–N(3)	2.4729(9)	Ca(1)–Ca(3)	3.4060(4)
Ca(3)–N(1)	2.4062(10)	Ca(1)–Ca(2)	3.4454(4)
Ca(3)–N(1)	2.4496(9)	Ca(1)–Ca(3)	3.4742(4)
Ca(3)–N(3)	2.4739(9)	Ca(2)–Ca(1)	3.2311(4)
Ca(3)–N(4)	2.4873(9)	Ca(2)–Ca(1)	3.2533(4)
Ca(3)–N(4)	2.5045(9)	Ca(2)–Ca(2)	3.3145(5)
Ca(4)–N(1)	2.4362(9)	Ca(2)–Ti(1)	3.3149(4)
Ca(4)–N(3)	2.4956(9)	Ca(2)–Ca(1)	3.4454(4)
Ca(4)–N(1)	2.5258(9)	Ca(2)–Ca(3)	3.4936(4)
Ca(4)–N(4)	2.5678(9)	Ca(2)–Ca(2)	3.5059(5)
Ca(4)–N(4)	2.5990(10)	Ca(4)–Ca(3)	3.4142(4)

determined using 124 well-centered reflections. After data collection, the systematic absences presented the possible space groups as $C2$ (chiral), Cm (non-centrosymmetric) and $C2/m$ (centrosymmetric) with initial R values for these monoclinic groups at $R_{\text{int}} = 0.0308$. The E -statistics function of the SHELX software suite indicated the probability of centrosymmetry at 61.5%. The crystal structure was solved in all three space groups using direct methods with the highest symmetry space group, $C2/m$, producing the best results. An initial solution suggesting the positions of two niobium atoms and six calcium atom positions was found using direct methods. Repeated least-squares refinement with Fourier difference maps determined that one of the niobium positions and two of the calcium positions

Table 5
 R_1 values and displacement parameters for varying occupancies of the N(2) position in Ca_5NbN_5

N(2) occupation	R_1	U (eq)*
100%	0.0254	0.03539
65.3% (freely refined)	0.0228	0.01180
50%	0.0238	0.00063

*The displacement parameters for the other four nitrogen atoms are 0.00758, 0.001979, 0.00977 and 0.01221.

were likely correct. The second niobium position was determined to be a calcium atom and an additional calcium position was located. The five nitrogen positions were then found. All positions were independently tested for partial occupancy, and all but one appeared to be fully occupied. One nitrogen position, N(2) freely refined to a partial occupancy of 65% (Table 5), but was assigned a 50% partial occupancy for charge balance. Anisotropic refinement was successfully applied to all atoms. The choice of the higher symmetry space group, $C2/m$, was confirmed and the crystallographic results are summarized in Table 1. The atomic coordinates were standardized; these and the anisotropic displacement parameters are shown in Tables 6 and 7, respectively. The R indices for the crystal structure solution are good, $R_1 = 0.0238$, $wR_2 = 0.0609$ for $I > 2\sigma(I)$ and $R_1 = 0.0250$, $wR_2 = 0.0614$ for all data, and the remaining largest difference peak and hole are small, 1.386 and $-0.811 \text{ e}^- \text{\AA}^{-3}$ respectively.

The Fourier difference peak and hole size indicate that all the electron density has been assigned to atoms with $Z \geq 3$, with only the possibility of unseen hydrogen in the structure. However, there was no indication of any hydrogen-containing impurities in the X-ray powder patterns of any of the starting materials, so hydrogen was excluded. The largest difference peak is less than that of the three electrons necessary for lithium. Nevertheless, because

Table 6
Atomic coordinates for Ca_5NbN_5

Atom	Wyckoff position	x	y	z	$U_{\text{eq}} \text{Å}^2 \times 10^3$
Nb(1)	4i	0.3701(1)	0	0.2265(1)	5(1)
Ca(1)	8j	0.1167(1)	0.2486(1)	0.1580(1)	13(1)
Ca(2)	4i	0.1363(1)	0	0.8345(1)	12(1)
Ca(3)	4i	0.2529(1)	0	0.5191(1)	11(1)
Ca(4)	4h	0	0.2476(1)	$\frac{1}{2}$	9(1)
N(1)	8j	0.3110(2)	0.2280(3)	0.3249(2)	9(1)
N(2)*	4i	0.0623(4)	0	0.3542(5)	2(1)
N(3)	4i	0.3231(3)	0	0.0066(3)	15(1)
N(4)	4i	0.5376(2)	0	0.3086(3)	10(1)
N(5)	2a	0	0	0	15(1)

*The N(2) position is 50% occupied.

Table 7
Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for Ca_5NbN_5

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Nb(1)	5(1)	5(1)	5(1)	0	1(1)	0
Ca(1)	9(1)	14(1)	16(1)	-6(1)	0(1)	0(1)
Ca(2)	18(1)	9(1)	13(1)	0	10(1)	0
Ca(3)	14(1)	7(1)	13(1)	0	8(1)	0
Ca(4)	6(1)	10(1)	8(1)	0	0(1)	0
N(1)	8(1)	10(1)	9(1)	0(1)	1(1)	0(1)
N(2)	1(2)	3(2)	4(2)	0	0(2)	0
N(3)	20(1)	16(1)	8(1)	0	-1(1)	0
N(4)	10(1)	11(1)	7(1)	0	2(1)	0
N(5)	12(2)	12(2)	22(2)	0	6(2)	0

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

of the use of lithium nitride as the reaction flux, there is always the possibility that small-size lithium atoms may have been included in the compound. Of the first 20 peaks of the Fourier map, one peak (in a special position: 0.5, 0.0, 0.0 with electron density of $0.99 \text{ e}^- \text{Å}^{-3}$) had a closest distance to the nearest atom (nitrogen) of 2.12 Å, a reasonable Li–N bond length. However, the refinement was unstable with the insertion of lithium in this position: after repeated least-squares refinements, the displacement parameter of this position stabilized at a value of 2.000 which is much too high for lithium as well as producing a non-positive anisotropic parameter. The above facts indicated an unlikely occupation of this position. The other 19 peaks of the Fourier map were all less than 1.6 Å from other positions (too short for bonds) with all but the first one having difference peaks of 0.99 or less. Fourteen of these Fourier difference peaks are within 1.3 Å of a niobium or calcium position and are likely the result of the truncation of the included diffraction peaks to $\theta < 30.50^\circ$.

The crystal structure of Ca_5NbN_5 is shown in Fig. 4. The structure contains a single niobium position, four calcium positions and five nitrogen positions. All positions are fully occupied except the nitrogen position N(2), which is 50% occupied. The niobium atoms are surrounded by nitrogen

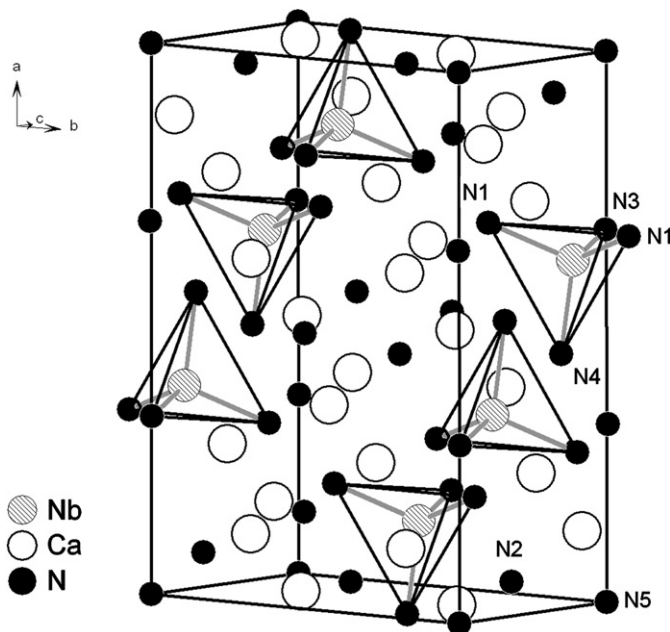


Fig. 4. Crystal structure of Ca_5NbN_5 showing the isolated NbN_4 tetrahedra and the five crystallographically different nitrogen positions. Niobium atoms are hatched, calcium atoms are open circles and nitrogen atoms are black.

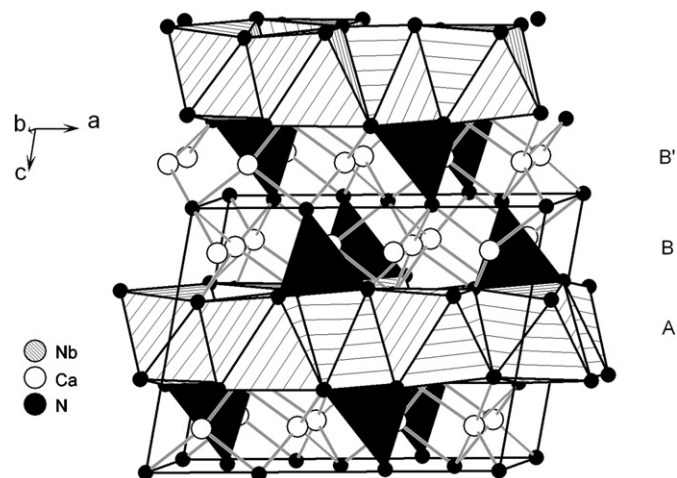


Fig. 5. View of Ca_5NbN_5 down the b -axis showing the two different cation layers. The A layer has edge-sharing CaN_6 octahedra. The B layers contain niobium and calcium polyhedra (Fig. 5). The first layer consists of calcium atoms Ca(3) and Ca(4) in chains of edge-sharing CaN_6 octahedra. The second layer contains the niobium tetrahedra which share three corners with CaN_5 trigonal bipyramids. Three trigonal bipyramids share

atoms in a regular tetrahedron; the tetrahedra are isolated from each other.

The structure can be described as having two main types of layers in an ABB' stacking. Viewed down the b -axis, the A layer contains only CaN_6 octahedra, and the B layers contain niobium and calcium polyhedra (Fig. 5). The first layer consists of calcium atoms Ca(3) and Ca(4) in chains of edge-sharing CaN_6 octahedra. The second layer contains the niobium tetrahedra which share three corners with CaN_5 trigonal bipyramids. Three trigonal bipyramids share

edges with each other in a triangular pattern, then share an additional edge with other sets of three (Fig. 6).

The most interesting atom position in the structure is the partially occupied nitrogen position, N(2). N(2) is bonded only to calcium atoms: two Ca(1), one Ca(2), one Ca(3) and finally two Ca(4). Interestingly, N(2) is not centered in the calcium environment; it is offset to one side. The bond lengths to the Ca(1) positions are 2.352 Å, the bond lengths to Ca(4) positions are 2.618 Å, and the bond lengths to Ca(2) and Ca(3) are 2.628 and 2.454 Å, respectively. Three of the four other crystallographically different nitrogen atom positions are also approximately octahedrally coordinated, the most typical coordination for nitrogen when very small atoms such as lithium are not present. N(1) is bonded to a niobium atom and calcium atoms Ca(1), Ca(2), Ca(4) and two Ca(3). N(4) is coordinated to one niobium atom, Ca(3) and two each of Ca(1) and Ca(4). The fifth nitrogen position, N(5), is bonded exclusively to calcium positions Ca(1) and Ca(2). Finally, the coordination sphere for nitrogen position N(3) includes only four atoms in a distorted tetrahedral environment. N(3) is bonded to one niobium atom with the shortest of the Nb–N bond distances at 1.934 Å. The shorter bond is reasonable in the tetrahedral environment where nitrogen has more electrons available. N(3) is also bonded to three calcium positions, Ca(1), Ca(1) and Ca(2) with Ca–N bond lengths among the shortest in the compound at 2.448–2.467 Å.

The Nb–N bond lengths in Ca_5NbN_5 range from 1.935–1.992 Å. For comparison, the average Nb–N bond distance for tetrahedrally coordinated niobium is 1.957 Å in Li_7NbN_4 [26], 1.948 Å in $\text{Li}_3\text{Ba}_2\text{NbN}_4$ [27], 1.975 Å in Sr_5NbN_5 [28] and 1.945 Å in $\text{Ba}_5\text{NbN}_{4.92}$ [29]. The first calcium position, Ca(1), is coordinated to all five crystal-

lographically unique nitrogen positions. The Ca–N bond distances range from 2.467–2.618 Å. The trigonal bipyramidal geometry for Ca(2) is similar; it is connected to N(2), N(3), N(5) and two N(1) positions. The Ca–N bond lengths are 2.401–2.628 Å. All of these bond distances are comparable to those for Ca_3N_2 in which the Ca–N bonds are between 2.453–2.482 Å [30].

The octahedrally coordinated calcium positions are Ca(3) and Ca(4). The *A* layer described above connects to the *B* layers through nitrogen positions N(1), N(1) and N(4); the CaN_6 octahedra share edges with the NbN_4 tetrahedra. Calcium position Ca(3) is in a regular octahedral environment while the octahedra for Ca(4) are slightly distorted. Ca(3) is bonded to four N(1) positions in one plane with Ca–N bond lengths of 2.535–2.538 Å and apical Ca–N bond distances of 2.454 and 2.668 Å for bonds to N(2) and N(4), respectively. Ca(4) is coordinated two N(1) positions, two N(2) positions and two N(4) positions with bond lengths ranging from 2.352–2.539 Å.

3.3. Further discussion of synthetic conditions

The synthesis and structural characterization of Ca_5NbN_5 was described above. The intention was to synthesize a new ternary calcium niobium nitride because only CaNbN_2 has been reported in the literature. Crystals of Ca_5NbN_5 were also found in reactions where niobium was not intentionally introduced but used as the reaction container. These experiments included the addition of zirconium and hafnium with lithium nitride and calcium nitride in two separate reactions heated to 900 and 1050 °C, respectively. In all three cases, crystals of Ca_5NbN_5 were found adhering to the inner walls of the niobium tubes. Hafnium reacted with available nitrogen and produced hafnium nitride; no other hafnium compound was detected. In the zirconium-containing reaction, additional crystals were found in the reaction tube; these were very small and yellow in color. Microprobe analyses indicated a Ca:Nb:Zr ratio of 20:4:1, but the CCD single-crystal analysis was unsuccessful: the crystals were either too small or too poorly crystalline to achieve data useful for structure solution.

3.4. Further discussion of crystal structure determination

Although the *R* indices for the crystal structure solution described above are good, and the remaining largest difference peak and hole are small, the structure is only charge balanced with assignment of partial occupancy to one of the nitrogen positions. The crystals of this compound are transparent orange in color and therefore it is likely that the cations are fully oxidized. The occupancy of nitrogen position N(2) was allowed to freely refine with the result of a 65% occupancy. At 50% occupancy of this position, the crystal is charge balanced. This solution is isostructural to $\text{Ba}_5\text{NbN}_{4.92}$ [29] which also was reported to refine to lowest *R* values with one partially

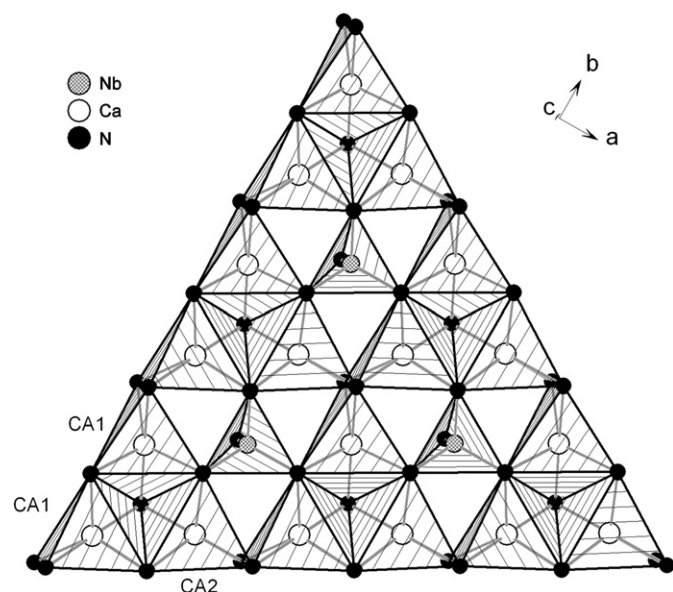


Fig. 6. Layer of edge-sharing CaN_5 trigonal bipyramids sharing vertices with NbN_4 tetrahedra viewed down the *c*-axis of Ca_5NbN_5 . Calcium atoms are open circles and nitrogen atoms are colored black.

occupied nitrogen position –47% occupancy. All positions, niobium, calcium and nitrogen, were allowed to freely refine (in separate experiments) for possible partial occupancy. The four other nitrogen positions and the niobium position indicated full occupancy. The four calcium positions returned occupancy values, of 97%, 96%, 95% and 97% which are close to indicating full occupancy.

There was another possible structure solution investigated which involved the presence of oxygen in the structure. It is extremely difficult to distinguish nitrogen and oxygen by X-ray techniques, especially in the presence of heavy atoms. As mentioned previously, electron microprobe analysis revealed the presence of a small amount of oxygen (approximately 5% of the nitrogen signal). This is not uncommon, because it is difficult to completely protect crystals from oxygen exposure while they are being analyzed in polybutene oil under the optical microscope or in transfer to the electron microprobe. Thus, a small oxygen signal is not a definitive indication of oxygen in the structure. In the structure refinement described above, though, the displacement parameter of the partially occupied nitrogen position, N(2), is quite low: 0.00063 when forced to 50% occupancy for charge balance. (At the freely refined value of 65%, the displacement parameter is in line with the other nitrogen positions, but the structure is not charge-balanced. Refer to Table 5 for relevant *R* factors of different models of N(2) site occupancy.). Therefore, the possibility of oxygen in the structure was tested. Only when oxygen was placed on the N(2) positions did the *R* factor improve. No other position other than N(2) improved with the replacement of nitrogen with oxygen or with a shared nitrogen/oxygen site. The N(2) position only improved when nitrogen was replaced with oxygen (50% occupancy) not when the position was shared. At 50% oxygen occupancy in this position, the compound would be short of negative charge. The occupancies of the cation positions were rechecked and again, niobium was 100% occupied and the calcium positions refined freely to 95–97% occupancy. At these occupancies, the structure does properly charge balance. Because the standard deviation of the occupancy values for calcium generally seems to approach $\pm 5\%$, the calcium positions can be considered fully occupied.

It is interesting to analyze the bond valence sums with regard to the question of oxygen vs. nitrogen occupancy using Eutax [17] (Table 8). With only nitrogen in the structure solution, the N(2) position has a considerably smaller bond valence sum of 2.375 than do the other nitrogen positions (N(1), N(3), N(4), and N(5) have values of 3.029, 2.666, 2.919 and 2.638, respectively). When oxygen is inserted in place of nitrogen in the N(2) position, a bond valence sum of 1.491 results. The other anion positions (all nitrogen) then have values of 3.031, 2.664, 2.921 and 2.639. Eutax does not have a parameter for partial occupancy, so the aforementioned values are all for fully occupied positions; the partial occupation of the N(2)

Table 8
Calculated bond valence sums and Madelung site potentials for Ca_5NbN_5

Element	Input charge	Bond valence sum	Potentials (V)
<i>With nitrogen in position N(2)</i>			
Ca(1)	+2	1.868	–19.052
Ca(2)	+2	1.947	–19.416
Ca(3)	+2	2.040	–22.909
Ca(4)	+2	2.601	–23.703
Nb	+5	5.013	–47.776
N(1)	–3	3.029	+33.587
N(2)	–3	2.375	+24.881
N(3)	–3	2.666	+36.840
N(4)	–3	2.919	+34.389
N(5)	–3	2.638	+30.683
<i>With oxygen in position “N(2)”</i>			
Ca(1)	+2	1.764	–20.336
Ca(2)	+2	1.851	–20.497
Ca(3)	+2	1.877	–22.458
Ca(4)	+2	2.181	–21.729
Nb	+5	5.019	–49.698
O	–2	1.491	+18.635
N(1)	–3	3.031	+32.904
N(3)	–3	2.664	+33.974
N(4)	–3	2.921	+33.277
N(5)	–3	2.639	+29.327

position is most likely responsible for lowering the values. For comparison of bond valence sums, the bond valence sums of calcium and nitrogen in Ca_3N_2 are 1.7 and 2.5 [31]; and are 1.773–2.084 and 2.588–3.116 in Ca_4TiN_4 , respectively. The bond valence sums for calcium and nitrogen are generally lower than the expected values of 2 and 3, respectively. Table 9 tabulates the bond valence sums and Madelung potentials for calcium, nitrogen as well as the transition metals or main group metals of 17 calcium nitride compounds.

The Madelung potentials for the N(2) position are also different from the other anion positions. For the nitrogen only solution, the potential for the N(2) position is +24.881 V compared to a range from +30.683 to +36.840 V for the other positions. In the oxygen-containing solution, the “N(2)” positions has a potential of +18.635 V compared to values of +29.327–33.974 V for the nitrogen positions. A Madelung potential of +20 V $\pm 10\%$ is almost universally found for oxygen.

Unfortunately, then, the bond valence sums and Madelung potentials don't help to decide between nitrogen and oxygen. Therefore, it is the WDX analysis that is most conclusive; the oxygen signal is much lower than what would be observed if oxygen was actually present on the N(2) position. If oxygen were present and no other oxygen contributed to the signal (i.e. no surface oxygen), the ratio of oxygen to nitrogen found by WDX should be 17% if the N(2) site was occupied at the 75% needed for charge balance, a value much larger than the 5% observed, which is likely due to surface oxygen and is nearly always observed in nitrides. For comparison, note the approximately 4% oxygen-to-nitrogen signal in Ca_4TiN_4 .

Table 9
Eutax-calculated bond valence sums and Madelung potentials of selected calcium nitride compounds

Compound	Calcium		Element <i>M</i>			Nitrogen	
	Bond valence sum	Madelung potential (V)	Assigned charge	B.V.S.	Madelung potential (V)	B.V.S.	Madelung potential (V)
CaMg ₂ N ₂	1.65	−19.59	+2	1.71	−23.08	2.54	+31.44
Ca ₄ TiN ₄	1.77–2.09	*	+4	3.76	*	2.59–3.12	*
Ca ₂ VN ₃	1.83–2.24	−(20.98–21.88)	+5	4.56	−55.42	2.70–3.08	+ (33.13–40.58)
Ca ₃ VN ₃	1.64	−(19.91–21.11)	+3	3.43	−36.39	2.64–3.09	+ (30.29–30.96)
Ca ₅ NbN ₅	1.87–2.60	−(19.05–23.70)	+5	5.01	−47.78	2.38–2.92	+ (24.88–36.84)
Ca ₃ CrN ₃	1.72–1.76	−(20.02–21.48)	+3	3.47	−36.66	2.77–3.13	+ (30.00–31.42)
Ca ₄ Cr ₂ N ₆	2.05–2.18	*	+5	4.64	*	2.82–3.09	*
Ca ₆ Cr ₂ N ₆ H	1.99	−21.37	+3, +4	3.23	−36.38	2.96	+32.57
Ca ₆ MnN ₅	1.69	−20.41	+3	4.07	−37.27	2.77–2.94	+ (28.88–31.15)
Ca ₂ FeN ₂	1.71–1.78	−(19.72–21.41)	+2	2.69	−25.81	3.07–3.10	+ (29.06–30.71)
CaNiN	1.51	−19.30	+1	1.81	−16.59	3.32	+29.82
Ca ₂ ZnN ₂	1.82	−21.89	+2	1.65	−21.48	2.64	+29.37
Ca ₂ GeN ₂	1.80–1.88	−(21.09–22.00)	+2	2.08	−20.54	2.87–2.89	+ (28.69–29.41)
Ca ₄ GeN ₄	1.73–2.17	−(20.01–21.84)	+4	3.70	−45.84	2.69–3.22	+ (31.74–32.46)
LiCaGaN ₂	2.12	−20.90	+3	2.53	−33.46	2.72–2.86	+ (32.95–33.57)
Ca ₂ InN	1.63–1.87	−(17.77–19.48)	−1	2.02, 2.61	+5.70	2.49	+29.53
Ca ₅ WN ₄ O ₂	1.77–2.00	−(20.24–23.36)	+6	6.49	−60.69	2.90–3.34	+ (34.15–35.89)
Oxygen						1.44–1.87	+ (17.64–20.64)

*Eutax cannot calculate Madelung potentials for triclinic structures such as these.

4. Conclusions

Two new ternary nitrides, Ca₄TiN₄ and Ca₅NbN₅, were synthesized using lithium nitride as a flux. Triclinic Ca₄TiN₄ is the first example of a calcium group IV nitride; it contains isolated tetrahedral TiN₄ units. Monoclinic Ca₅NbN₅ is isostructural with Ba₅NbN₅; the structure contains NbN₄ tetrahedra that share vertices with CaN₅ trigonal bipyramids.

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