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# Synthesis and Structure of the New Ternary Nitride $SrTiN_2$

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A new ternary nitride, $SrTiN_2$, has been synthesized by the solid-state reaction of $Sr_2N$ with TiN and characterized by powder X-ray diffraction. $SrTiN_2$ crystallizes in the tetragonal space group $P4/nmm$ ($a = 3.8799(2)$ Å, $c = 7.6985(4)$ Å, $Z = 2$) and is isostructural with $KCoO_2$. Titanium is coordinated to five nitrogens in a distorted square-based pyramidal geometry, forming layers of edge-sharing pyramids which stack along the (001) direction. Strontium is situated between the Ti−N layers and is coordinated to five nitrogen atoms. The title compound is only the third example of a ternary titanium nitride.

## Introduction

In the past several years there has been a renewed interest in the chemistry of the ternary and higher order transition metal nitrides, with much discussion and speculation regarding their physical properties and potential applications. The ternary nitrides exhibit a wide range of diverse and often novel crystal structures, and preparative routes are often practically difficult.[1−4]

In some of these structures, transition metal ions display unusual coordinations to nitrogen which are rarely found outside ternary nitride chemistry. Examples are the families of ternary phases $A_3MN_3$ (313)[3−8] (A = alkaline earth; M = V, Cr, Mn, Fe) and $Ca_6MN_5$ (615)[9,10] (M = Fe, Ga, Mn). Both contain $M^{3+}$ coordinated to three nitrogens and have structures consisting of sheets of carbonate-like $[MN_3]^{6-}$ planar triangular units separated by alkaline earth cations. Nitrides can also adopt structures seen in carbide and oxide chemistry. For instance, CaNiN has the YCoC structure containing chains of linear Ni−N units that run perpendicular to the long $c$ axis.[11] $Ba_2VN_3$ is one of an increasing number of nitrides with a ternary oxide structure. It exists with the orthorhombic $Rb_2TiO_3$ structure containing chains of corner-sharing $[VN_3]^{4-}$ tetrahedra.[12]

Ternary nitrides of the stoichiometry $AMN_2$ (A = alkali metal, alkaline earth metal, or transition metal; M = transition metal or lanthanide) have already been observed to crystallize in a variety of different structures. $LiMN_2$ (M = Mo, W) are hexagonal layered compounds with Mo or W coordinated to six nitrogens in trigonal prismatic coordination.[13,14] These nitrides are reported to be paramagnetic and metallic in nature. The alkali metal nitrides $ATaN_2$ (A = K, Rb, Cs) have structures related to that of $\beta$-cristobalite whereas the ternary nitrides $NaMN_2$ (M = Nb, Ta) have the layered $\alpha$-$NaFeO_2$ structure.[15,16] In the latter materials both cations are coordinated to nitrogen in an octahedral geometry. Mixed transition metal nitrides such as the family $MWN_2$ (M = Mn, Co, Ni, Fe),[17−19] are layered materials similar in structure to $LiMoN_2$ with alternating layers of A−N octahedra and M−N trigonal prisms. As with $LiMoN_2$, these materials are metallic and paramagnetic. The copper nitridotantalate $CuTaN_2$, however, crystallizes in the $\alpha$-$CuFeO_2$-type (delafossite) structure.[20]

Of the alkaline earth nitrides, $BaCeN_2$ is another layered material, isostructural with $\beta$-$RbScO_2$ and with Ce in octahedral coordination.[21] $BaZrN_2$, isostructural with $KCoO_2$,[22] is also layered, but in this instance, the layers are composed of edge-sharing Zr−N square-based pyramids.[23] Interestingly, this material is reported to show temperature-independent paramagnetic behavior between 20 and 300 K. The strontium ternary nitrides $SrZrN_2$ and $SrHfN_2$ both adopt the $\alpha$-$NaFeO_2$ structure,[24] as does $CaTaN_2$.[25] While the former materials appear to be intrinsically diamagnetic, the nitridotantalate has aroused considerable interest because of the superconducting transition observed at ca. 9.6 K.

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We are currently involved in extensive research into the structures and properties of ternary transition metal nitrides. In this paper, we report the synthesis and structural determination of the new layered $AMN_2$ ternary nitride $SrTiN_2$.

## Experimental Section

**Starting Material.** The starting material $Sr_2N$ was prepared by the reaction of the molten alkaline earth metal−sodium alloy with dried nitrogen at 520 °C. Molten alkali and alkaline earth metals are highly reactive to air and water, and these were handled under inert atmospheres at all times. The alloy was prepared by adding clean Sr metal to molten sodium in a stainless steel crucible at 250 °C in an argon-filled glovebox. The cooled crucible of alloy was contained in a stainless steel vessel and heated to 520 °C under a positive pressure of nitrogen, monitored by a pressure transducer, until the gas pressure remained constant. Excess sodium was removed by heating under vacuum at 400 °C for 24 h. Liquid sodium is unreactive toward nitrogen and serves as an inert solvent for the alkaline earth metals. This method produced strontium nitride ($Sr_2N$) containing negligible amounts of the alkaline earth oxide. The reaction yielded crystalline samples of purple-black $Sr_2N$. The identity of $Sr_2N$ was confirmed by powder X-ray diffraction (PXD).

**Synthesis of $SrTiN_2$.** A polycrystalline sample of $SrTiN_2$ was prepared by the high-temperature solid-state reaction of the binary alkaline earth nitride and titanium nitride (TiN) (99%) powders. All preparations were carried out in a purified-argon-filled glovebox. The $Sr_2N$ and TiN powders were thoroughly mixed, ground together in a 1:1 molar ratio, and pelleted using a hand press. The pellet was wrapped in a molybdenum foil tube and placed within a stainless steel crucible which was subsequently welded closed under purified argon. The stainless steel crucible was fired in a tube furnace at 1030 °C for 5 days under flowing argon to prevent oxidation of the steel and then cooled at 20 °C/h to room temperature, again under flowing argon. The outer surface of the cooled crucible was mechanically cleaned to remove any oxidized steel. The cleaned crucible was then cut open in a nitrogen-filled glovebox. There was no apparent reaction of the nitride with the Mo tube, and the resulting powder of $SrTiN_2$ was black.

**Characterization and Structure Determination.** PXD data were collected using a Philips XPERT $\theta-2\theta$ diffractometer with Cu K$\alpha$ radiation. In each case, the sample was loaded in a nitrogen-filled glovebox onto an aluminum slide contained in an aluminum holder with a Mylar film window and threaded removable cover with an O-ring seal.[8] This arrangement allowed powder data of air-sensitive materials to be collected without Mylar peaks appearing in the diffraction pattern. Initially, ca. 60 min scans were taken of each sample over a $2\theta$ range of 5−80° to assess sample purity and to determine lattice parameters. Purity was assessed by using the IDENTIFY routine as part of the Philips diffraction software package on a PC which allows access to the JCPDS database. The sample of $SrTiN_2$ was shown to contain small amounts of SrO and Sr metal. These impurities are to be expected from the starting ratio which generates Sr as an additional product. The remaining peaks of each pattern were indexed by using a combination of the PC software programs VISSER,[26] DICVOL91,[27,28] and TREOR90.[29] Lattice parameters were refined by least-squares fitting of PXD data.

The space group was deduced to be one of several higher symmetry tetragonal groups by considering the observed reflections and systematic absences, but an eventual starting model was obtained by comparison with a theoretical powder pattern based on $BaZrN_2$ (crystallizing in the space group $P4/nmm$) generated by LAZY PULVERIX.[30] A convincing agreement was reached by substituting the refined lattice parameters and Sr and Ti for Ba and Zr, respectively.[23] This structure is isotypic with that reported for $KCoO_2$, with the crystallographic description differing only in the placement of the origin of the unit cell.[22] Diffraction data suitable for Rietveld refinement were collected over the range 5−125° $2\theta$ with step size 0.02° $2\theta$. Scans were run for approximately 14 h. A full-profile Rietveld refinement[31] of $SrTiN_2$ was performed using the Philips PC RIETVELD PLUS[32,33] package with the $BaZrN_2$ structure as an initial model and with cell parameters obtained from least-squares fitting of PXD data. Peak shapes were modeled using the pseudo-Voigt function, and the background was entered manually.

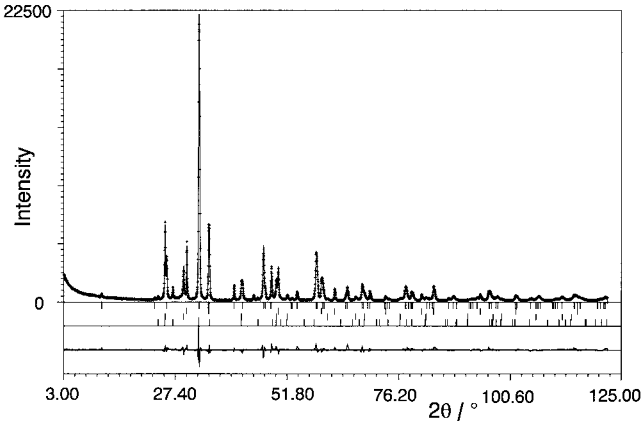

**Figure 1.** Observed, calculated, and difference plots for $SrTiN_2$. (Contributions to the profile from impurity phases are also shown, indicated by tick marks for phases 2−4.)

Initial cycles in the refinement of $SrTiN_2$ allowed for the variation of the scale factor, zero point, and lattice parameters. As the refinement progressed, atomic positions and peak width parameters were introduced. In final cycles, isotropic temperature factors were introduced. Attempts to introduce anisotropic temperature factors were unsuccessful without destabilizing the refinement. Variation of the N2 isotropic temperature factor led to a consistent small negative value being observed. This was set to a low positive value, similar in magnitude to the N1 site temperature factor, without increasing $R$ factors. Impurity phases of SrO, Sr, and $\alpha$-Sr were simultaneously refined, and quantitative analysis of the diffraction data running as part of the PC RIETVELD PLUS package yielded weight percentage values of 12.5% SrO, 2.6% Sr, and 14.3% $\alpha$-Sr, respectively. Observed, Calculated, and difference plots for the refinement of $SrTiN_2$ are shown in Figure 1.

Qualitative atomic absorption (AA) analysis for possible transition metal impurities revealed the presence of trace amounts of iron, chromium, and nickel. The origin of these impurities is possibly from the stainless steel crucible. A more likely source, given the observed concentrations, is probably from impurities in the TiN starting material. None of these transition metal phases were present in sufficient concentrations to be detectable by powder X-ray diffraction. Indeed, crude calculations from the AA results suggest concentrations of $\ll 1$ wt %.

## Results and Discussion

The final crystallographic results for $SrTiN_2$ are shown in Table 1. $SrTiN_2$ (Figure 2) is isotypic with $KCoO_2$ and $BaZrN_2$.[22,23] The structure consists of $[TiN_2]^{2-}$ anions and $Sr^{2+}$ cations. The nitridotitanate anions are composed of Ti atoms surrounded by nitrogens in a 5-fold, square-based pyramidal coordination. Each square-based pyramid has a bent basal plane and overall $C_{4v}$ point symmetry. The $[TiN_2]^{2-}$ square-based pyramidal anions are linked by the edges of the pyramid bases to form layers in which the apexes of adjoining pyramids are

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**Table 1.** Final Crystallographic Results for $SrTiN_2$

| atom | site | *x* | *y* | *z* | $B^a$/Å$^2$ | *N* |
|---|---|---|---|---|---|---|
| Sr | 2c | 0.25 | 0.25 | 0.8372(1) | 0.42(1) | 1.0 |
| Ti | 2c | 0.25 | 0.25 | 0.4115(2) | 0.14(3) | 1.0 |
| N1 | 2b | 0.75 | 0.25 | 0.5 | 0.3(2) | 1.0 |
| N2 | 2c | 0.25 | 0.25 | 0.1725(9) | 0.4 | 1.0 |

space group *P*4/*nmm*, $a = 3.8799(2)$ Å, $c = 7.6985(4)$ Å
$R_I = 3.67\%$, $R_p = 6.54\%$, $R_{wp} = 8.58\%$, $R_e = 1.34\%$

[a] $B = {}^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

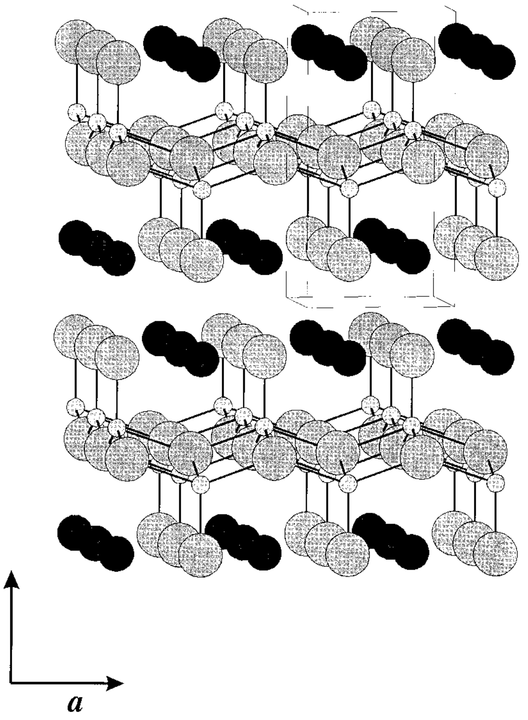

**Figure 2.** Structure of $SrTiN_2$. Sr atoms are shown as medium spheres, Ti as small spheres, and N as large spheres. N1 atoms form the bases of Ti−N pyramids, and N2 atoms the apexes. The unit cell is indicated by the dashed lines.

aligned alternately "up" and "down" parallel to the *c* axis (Figure 3). The $Sr^{2+}$ cations are situated between these Ti−N sheets level with the pyramid apexes. Important interatomic distances in $SrTiN_2$ are shown in Table 2. Bond angles around the metal atoms and nitrogen atoms are described in Tables 3 and 4, respectively.

The square-based pyramidal nitridotitanate anions are compressed along the *c* axis, resulting in one shorter apical Ti−N2 bond at 1.839(7) Å and four longer basal Ti−N1 bonds at 2.0561(7) Å. The basal nitrogens are bent away from the plane of the titanium to produce an N1−Ti−N1 angle of significantly less than 180° (~141.3°). The central Ti atom consequently sits ≈0.68 Å above the plane of the basal nitrogens. This is an arrangement similar to that observed in the nitridozirconate anions in $BaZrN_2$, where the apical distances of the pyramids were also shorter than the basal metal−nitrogen bonds.[23] As in the nitridozirconate, whereas the basal bonds are typical of a metal−nitrogen bond on the basis of ionic radii, the much reduced length of the apical metal−nitrogen distance suggests a multiple Ti−N bond. It is interesting to note that in $KCoO_2$—the oxide analogue of these group IV nitrides—there is no significant distortion of the $[CoO_2]^-$ pyramids. In $KCoO_2$, the apical Co−O bond (1.99 Å) and the basal Co−O bonds (1.91 Å) are nearly identical.[22]

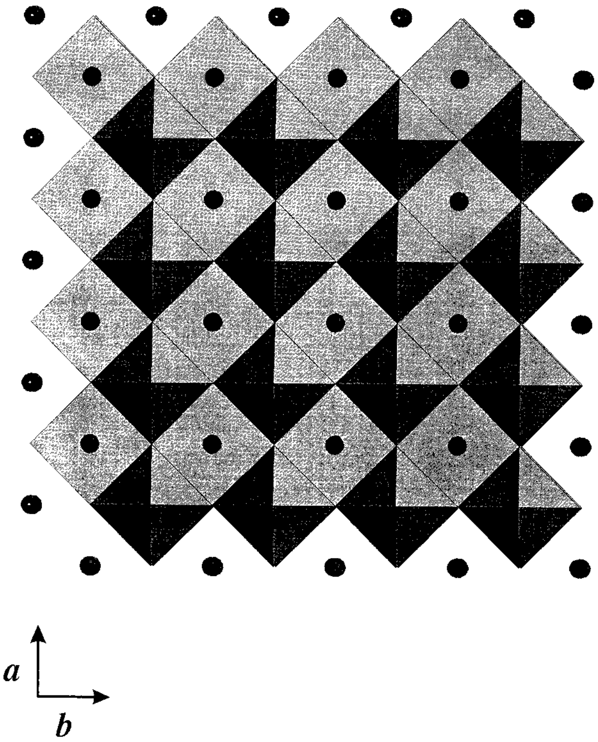

**Figure 3.** Structure of $SrTiN_2$ viewed in the *ab* plane showing alignment of alternate edge-linked $[TiN_2]^{2-}$ square pyramidal anions "up" and "down" the *c* axis.

**Table 2.** Interatomic Distances in $SrTiN_2$

| atoms | no. | distance/Å | atoms | no. | distance/Å |
|---|---|---|---|---|---|
| Sr−N1 | 4 | 3.2412(8) | Ti−N2 | 1 | 1.839(7) |
| Sr−N2 | 1 | 2.581(7) | Sr−Ti | 1 | 3.277(1) |
| Sr−N2 | 4 | 2.7445(2) | Sr−Ti | 4 | 3.345(1) |
| Ti−N1 | 4 | 2.0561(7) | Ti−Ti | 4 | 3.063(1) |

**Table 3.** Bond Angles (deg) around Sr and Ti in $SrTiN_2$

| | | | |
|---|---|---|---|
| N1−Sr−N1 | 73.529(3) × 2 | N2−Sr−N2 | 89.956(6) × 4 |
| N1−Sr−N1 | 50.076(2) × 4 | N2−Sr−N2 | 91.58(15) × 4 |
| N1−Sr−N2 | 113.63(14) × 8 | N1−Ti−N1 | 83.693(3) × 4 |
| N1−Sr−N2 | 63.56(13) × 8 | N1−Ti−N1 | 141.297(11) × 2 |
| N1−Sr−N2 | 143.236(1) × 4 | N1−Ti−N2 | 109.351(6) × 4 |
| N2−Sr−N2 | 176.82(22) × 2 | | |

**Table 4.** Bond Angles (deg) around N1 and N2 in $SrTiN_2$

| | | | |
|---|---|---|---|
| Sr−N1−Sr | 129.924(9) × 4 | Ti−N1−Ti | 141.29(6) × 2 |
| Sr−N1−Sr | 73.529(15) × 2 | Sr−N2−Sr | 88.41(2) × 4 |
| Sr−N1−Ti | 74.60(3) × 8 | Sr−N2−Sr | 89.956(1) × 4 |
| Sr−N1−Ti | 72.58(4) × 4 | Sr−N2−Sr | 176.82(5) × 2 |
| Sr−N1−Ti | 146.11(4) × 4 | Sr−N2−Ti | 91.58(2) × 4 |
| Ti−N1−Ti | 96.304(19) × 4 | Sr−N2−Ti | 180.00(7) |

The nature of the Ti−N bonding in nitridotitanates can vary significantly between systems. Single, σ-type, Ti−N bonds are typically of the order of 2.2 Å in molecular solids whereas multiple Ti−N bonds are considered to lie in the range 1.7−1.9 Å.[34,35] Ti−N bond lengths are consistently shorter than 2.2 Å in the solid state. Binary titanium nitrides exhibit Ti−N distances of ca. 2.1 Å, and the bonding can be viewed predominantly as σ-type. The average Ti−N bond length in $SrTiN_2$ is 2.012(2) Å, and this is considerably shorter than the Ti−N distance in $Ti_{0.72}N$ (2.118(1) Å), which contains essentially Ti(IV).[36] The mean Ti−N bond length in $SrTiN_2$

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(34) P. Mountford, personal communication.

(35) See, for example: Zambrano, C. H.; Profilet, R. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1993**, *12*, 689.

compares slightly more favorably, however, to those mean Ti−N distances reported in the various forms of $Ti_2N$ (2.070−2.078 Å).[37−39] The basal bond distances of the Ti−N pyramids in $SrTiN_2$ (2.0561(7) Å) are in particularly good agreement with the distances seen in $Ti_2N$, which, by contrast, emphasizes the multiple nature of the apical bond.

The number of known ternary nitridotitanates is small, and only one ternary alkaline earth titanium nitride, $Ba_{10}Ti_4N_{12}$, has been previously reported.[40] The titanium coordination in this compound is tetrahedral; four $TiN_4$ tetrahedra are vertex-connected to form unusual cyclic nitridotitanate(IV) anions. The average Ti−N bond length in $Ba_{10}Ti_4N_{12}$ is 1.95(4) Å, smaller than that in $SrTiN_2$. The bond lengths in the barium material lie in the relatively narrow range 1.92−1.99 Å, suggesting that all of the bonds show $\pi$-character. The only reported alkali metal ternary nitride is $Li_5TiN_3$.[41] The average bond length in $Li_5TiN_3$ is 2.02 Å, marginally larger than the mean Ti−N distance in the barium ternary nitride but very similar to the mean Ti−N bond length in $SrTiN_2$. At this stage, it is perhaps worth drawing attention to the short Ti−Ti distances (3.063(1) Å) in $SrTiN_2$, which are only slightly longer than the intermetallic distances seen in Ti metal (α-Ti, ∼2.90 Å; $\beta$-Ti, ∼2.87 Å)[42,43] and binary titanium nitrides (∼2.85 to ∼2.99 Å)[36−39] and shorter than the distances in the other known ternary compounds $Li_5TiN_3$ (∼3.43 Å)[41] and $Ba_{10}Ti_4N_{12}$ (∼3.75 Å).[40]

The coordination of strontium to nitrogen could be viewed as 9-fold, as for barium in $BaZrN_2$,[23] but is effectively only 5-fold with the longer "basal" distances of the Sr−N polyhedron being over 3.2 Å (3.2412(8) Å). The coordination geometry thus simplifies to a square-based pyramidal arrangement. The average Sr−N bond length, including the four longer distances, is 2.947(1) Å, whereas, excluding these distances, it is a more reasonable 2.711(2) Å. This distance is longer than the mean Sr−N distance observed in $Sr_2N$ (2.6118(3) Å),[44] as is frequently the case for Sr−N bonds in ternary strontium nitrides. The mean Sr−N distance is in better agreement with those observed in other ternary strontium phases, for example, 2.723(9) Å in $Sr_3MnN_3$[6] and 2.739(1) Å in $Sr_3CrN_3$.[8]

The nitrogen atoms are coordinated to four and six metal atoms, respectively. N1 is coordinated in a distorted tetrahedral geometry to four titanium atoms and N2 in a distorted octahedral geometry to five strontium and one titanium atoms. The N2−M octahedron is compressed along *z*. The compression of the anion- and cation-centered polyhedra along *z* is reflected in the $c/a$ ratio (1.98) compared to those of $BaZrN_2$ (2.02) and $KCoO_2$ (2.08).[22,23]

Bond valence calculations have been performed for $SrTiN_2$ using the bond length parameters proposed by Brese and O'Keeffe for compounds with anions other than oxygen, fluorine, or chlorine.[45,46] The bond valence parameters used for Sr−N and Ti−N were 2.23 and 1.93 Å, respectively. The calculations yielded site valences of 1.38(1), 4.12(3), 2.84(1), and 2.66(3) for Sr, Ti, N1, and N2, respectively. Although the site valence for N2 is a little low, the most noticeable result of the bond valence calculations is the very low value for the Sr site. Whereas the Sr site valence increases to 1.64(1) if the Sr−N interactions at 3.2 Å are taken into account, the oxidation state is still less than the expected +2. The other effect of considering these interactions is to increase the N1 site valence to 3.10(1). Alkaline earth site valences (especially those of Sr and Ba) are frequently observed to be lower than expected in binary and ternary nitrides. This suggests either that the A−N bonds are longer than expected or that the formal oxidation state is lower than expected. This latter possibility is suggested for $Sr_2N$, where the stoichiometry would imply an oxidation state of 1.5 and bond valence calculations led to a low value similar to that of the Sr site in $SrTiN_2$ above.[44]

The Ti site valence is a little high, and this is generally seen for transition metal sites in ternary nitrides. This can usually be attributed to one or more multiple M−N bonds giving rise to distances that are shorter than expected. The N site valences are both lower than expected, but it is worth noting that N1 (bonding only to Ti) has the more reasonable oxidation state. Bond valence sums calculated from the crystallographic data for $BaZrN_2$[23] are higher than those in $SrTiN_2$ for both the two cation and two anion sites. The calculated site valences are 1.74(2), 4.4(1), 3.34(2), and 2.8(1) for the Ba, Zr, N1, and N2 sites, respectively. Significantly, the alkaline earth (Ba) site valence is lower than expected and the N2 site is slightly below 3, but otherwise the values are higher than the anticipated oxidation states, implying unusually short, multiple M−N bonds.

Particularly in the light of the superconducting behavior recently observed in $CaTaN_2$,[25] there is a need for further investigation of the properties of $SrTiN_2$ and other group IV and V ternary nitrides if we are to fully understand how their structures and magnetic behaviors are interrelated. We are currently investigating the magnetic and electronic properties of these materials.

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**Supporting Information Available:** Listings of X-ray diffraction data for $SrTiN_2$, including *d* spacings, observed and calculated intensities, and indexed reflections, and of the final cycles in the refinement of $SrTiN_2$ showing final crystallographic parameters and esd's (8 pages). Ordering information is given on any current masthead page.

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