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Synthesis and Structure of Sr_2VN_3 and Ba_2VN_3, Two New Nitridovanadates

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Two new ternary nitrides, Sr_2VN_3 and Ba_2VN_3, have been synthesized by the solid state reaction of Sr_2N or Ba_3N_2 with VN in sealed stainless steel crucibles and characterized by powder X-ray diffraction. Sr_2VN_3 crystallizes in the space group *C2/c* (a = 5.71036(9) Å, b = 10.9521(2) Å, c = 12.2881(2) Å, β = 90.986(1)°, Z = 8) and is isostructural with Sr_2TaN_3. Ba_2VN_3 crystallizes in the space group Cmca (a = 5.8614(4) Å, b = 11.4682(7) Å, c = 12.9121(9) Å, Z = 8) and is isostructural with Rb_2TiO_3. In each structure vanadium (V) is coordinated to nitrogen in distorted tetrahedra, forming infinite one-dimensional chains of $[VN_3]^{4-}$ units running parallel to *a*. The strontium and barium atoms in these A_2VN_3 materials (A = Sr, Ba) are coordinated to seven nitrogens. These materials are the first reported group II ternary nitrides to contain V^{5+}.

Introduction

Until recently, relatively little was known of the chemical and physical properties of the ternary and higher order nitrides. Of these materials, still less is known of the chemistry of ternary nitrides formed from alkaline earth and transition metal ions. Within the last four years or so, several groups have reported preparative routes to these new materials and have described the large array of often novel crystal structures adopted by these phases.[1−4] Transition metal ions can display a range of different and unusual coordinations to nitrogen in ternary nitride structures. Materials of the compositions A_3MN_3 (313)[3−7] and A_6MN_5 (615)[8] (where A = alkaline earth, M = transition metal) contain sheets of $[MN_3]^{6-}$ planar triangular units separated by alkaline earth cations whereas nitrides such as BaNiN,[9] CaNiN,[10] and Ca_2ZnN_2[11] contain essentially linear two-coordinate metal−nitride groups linked in chains. Transition metals can adopt four-coordinate geometries with nitrogen in distorted tetrahedra such as in $Sr_3Al_2N_4$[12] where AlN_4 units form edge-sharing infinite chains.

We are currently involved in extensive research into new ternary nitrides with the intention of relating the physical properties of these materials to their crystal chemistry. Here we report the synthesis and structural characterization of two new nitridovanadates containing corner-sharing chains of distorted MN_4 tetrahedra. Sr_2VN_3 has the Ba_2ZnO_3[13] structure and is isotypic with Sr_2TaN_3, Ba_2TaN_3,[14] and the recently reported nitridoniobate Ba_2NbN_3.[15] Ba_2VN_3 has the Rb_2TiO_3[16] structure—a structure previously unseen in ternary nitrides. These materials are the first ternary group II nitrides reported to contain V in the +5 state, an unusually high oxidation state for first-row transition metal ions in ternary nitrides.

Experimental Section

Starting Materials. The starting materials Sr_2N and Ba_3N_2 were 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 in inert atmospheres at all times. The alloy was made by adding clean Sr or Ba 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 until the gas pressure remainded constant. The gas pressure was monitored with a pressure transducer throughout this process. Excess sodium was removed by heating under vacuum at 350 °C for 24 h. Liquid sodium is unreactive toward nitrogen and serves as an inert solvent for the alkaline earth metals. This method was found to produce nitrides containing negligible amounts of alkaline earth oxide. The reactions yielded crystalline samples of purple-black Sr_2N and dark red-black Ba_3N_2. The identity of the starting materials was confirmed by powder X-ray diffraction (PXD).

Synthesis of Sr_2VN_3 and Ba_2VN_3. Polycrystalline samples of A_2VN_3 (A = Sr, Ba) were prepared by the high-temperature solid state reaction of the binary alkaline earth nitride (Sr_2N or Ba_2N_3) and vanadium nitride (VN) (98.5%) powders. All preparations were carried out in an argon-filled glovebox. The alkaline earth nitride and VN powders were thoroughly mixed, ground together, and pelleted using a hand press. For A = Ba the reactants were mixed together in a 1:1 molar ratio whereas for A = Sr an excess of Sr_2N (2:1 molar ratio with VN) was used. The pellets were wrapped in molybdenum foil tubes and placed in stainless steel crucibles which were welded closed under argon. The crucibles were 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 cooled crucibles were cleaned and opened in a nitrogen-filled glovebox. There was no apparent reaction of nitrides with the Mo tubes. The resulting powders of Sr_2VN_3 and Ba_2VN_3 were red-brown and tan, respectively.

Magnetic Susceptibility Measurements. Simple magnetic susceptibility measurements were carried out at room temperature using a

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Johnson Matthey magnetic susceptibility balance. Samples were ground and loaded into preweighed sample tubes in an argon-filled glovebox. The tubes were filled to a height of ca. 1.5 cm and sealed. A molar susceptibility, χ_M, of -4.025×10^{-4} emu was obtained for Sr_2VN_3, indicating the nitride is diamagnetic and contains V^{5+}. Ba_2VN_3 gave a slightly higher value, $\chi_M = -1.763 \times 10^{-3}$ emu, also confirming the presence of V^{5+} as expected from the nominal stoichiometry.

Characterization and Structure Determination. PXD data were collected using a Philips XPERT $\theta-2\theta$ diffractometer with Cu Kα radiation. In each case, the sample was loaded under nitrogen onto an aluminium slide contained in an aluminium holder with a Mylar film window and threaded removable cover with an O-ring seal. 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 2θ 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. Samples of Sr_2VN_3 and Ba_2VN_3 were shown to contain SrO and BaO, respectively. The former nitride also contained a small amount of Sr metal. Excess metal phases would be expected from the starting stoichiometries. The remaining peaks of each pattern were indexed using a combination of the PC software programs VISSER,[17] DICVOL91,[18,19] and TREOR90.[20]

Space groups were derived from special absences, and cell parameters were refined by least-squares fitting. Sr_2VN_3 was found to be monoclinic (*C*2/*c*) and deduced to be isostructural with Ba_2TaN_3 by comparison with a theoretical powder pattern generated by LAZY PULVERIX.[21] The structure of Ba_2VN_3 was derived by direct methods using the PC package SIRPOW[22] working in the space group *Cmca* and using the calculated cell parameters from least-squares fitting. Diffraction data for use with SIRPOW were collected over the range 5−120° 2θ with step size 0.02° 2θ run for approximately 4 h. Observed profile intensities were extracted from the relevant output file from the Philips PC RIETVELD PLUS[23,24] package and converted to F^2 values for use with SIRPOW. Given the calculated lattice parameters, space group, and symmetry information and the number of atoms in the unit cell, SIRPOW generated atomic positions and temperature factors for Ba_2VN_3 ($R(F) = 9.46\%$, $R_w(F) = 9.69\%$). Ba_2VN_3 was found to be isostructural with Rb_2TiO_3[16] with Ba and V in the Rb and Ti positions, respectively, and N situated in the three oxygen positions. These equivalent positions were used as a basis for later Rietveld refinement.

Diffraction data suitable for Rietveld refinement were collected over the range 5−120° 2θ with step size 0.02° 2θ. Scans were run for approximately 14 h. Full profile Rietveld refinements[25] of Sr_2VN_3 and Ba_2VN_3 were performed using the Philips PC RIETVELD PLUS[23,24] package with the Sr_2TaN_3 and Rb_2TiO_3 structures, respectively, as initial models and with cell parameters obtained from least-squares fitting of PXD data. The structural data generated by SIRPOW were used in the initial refinement cycles for Ba_2VN_3. Peak shapes were modeled using the pseudo-Voigt profile function in both refinements. Initial cycles in the refinement of Sr_2VN_3 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 vary temperature factors of atomic sites anisotropically were unsuccessful. Variation of isotropic temperature factors for the N2, N3, and N4 positions led to a destabilization in the refinement and an oscillation of *B* values around a median point. These temperature factors were therefore set to a fixed value without significantly reducing *R* factors. Impurity phases of Sr and SrO were simultaneously refined.

Table 1. Final Crystallographic Results for Sr_2VN_3

space group *C*2/*c*, $a = 5.71036(9)$ Å,
$b = 10.9521(2)$ Å, $c = 12.2881(2)$ Å, $\beta = 90.986(1)°$

atom[a]	site	*x*	*y*	*z*	*B*, Å^2
Sr1	8f	0.2547(3)	0.3892(1)	0.0766(1)	1.25(4)
Sr2	8f	0.2431(4)	0.1986(1)	0.3531(1)	1.31(4)
V	8f	0.2452(6)	0.5016(3)	0.3373(3)	0.98(7)
N1	8f	0.286(2)	0.158(1)	0.1359(9)	0.6(2)
N2	4e	0	0.439(1)	0.25	0.20
N3	4e	0.5	0.477(1)	0.25	0.20
N4	8f	0.270(2)	0.406(1)	0.4524(8)	0.20

$R_I = 8.25\%$, $R_p = 6.74\%$, $R_{wp} = 9.07\%$, $R_e = 1.12\%$

[a] All site occupancies: 1.0.

Table 2. Final Crystallographic Results for Ba_2VN_3

space group *Cmca*, $a = 5.8614(4)$ Å,
$b = 11.4682(7)$ Å, $c = 12.9121(9)$ Å

atom[a]	site	*x*	*y*	*z*	*B*, Å^2
Ba1	8f	0	0.0557(3)	0.1457(3)	1.7(2)
Ba2	8f	0	0.8565(2)	0.4231(3)	1.3(1)
V	8f	0	0.249(1)	0.336(1)	2.7(3)
N1	8f	0	0.358(3)	0.437(3)	0.05
N2	8f	0	0.091(3)	0.364(3)	0.05
N3	8e	0.25	0.270(2)	0.25	0.05

$R_I = 10.07\%$, $R_p = 13.65\%$, $R_{wp} = 17.64\%$, $R_e = 1.73\%$

[a] All site occupancies: 1.0.

Collection of diffraction data for Ba_2VN_3 suitable for Rietveld refinement was complicated by the reactivity of Ba_2VN_3 toward water in air. Despite using "airtight" X-ray containers, Ba_2VN_3 was found to react with air in the time scale of the diffraction experiment (ca. 14 h scan). It is likely that air had permeated the Mylar film window. This reaction yielded β-barium hydroxide identified from its powder pattern in the JCPDS database.[26] β-$Ba(OH)_2$ could not be refined as an impurity phase in the diffraction pattern since the crystal structure is unknown. Attempts to exclude the β-$Ba(OH)_2$ peaks from the pattern were only of limited success and could not allow for the many overlapping Ba_2VN_3/β-$Ba(OH)_2$ peaks observed. In an effort to reduce β-$Ba(OH)_2$ production, shorter scans (ca. 4 h) were attempted over a similar 2θ range. These scans contained much lower amounts of the hydroxide, but diffraction data were of poorer quality (poorer peak shape, lower peak intensities) and did not lead to improvements in final *R* factors. "Best" results were finally obtained from 14 h scans (5−130° 2θ) where nonoverlapping β-$Ba(OH)_2$ peaks were excluded from the refinement. The significance of the overlapping β-$Ba(OH)_2$ peaks is reflected in the magnitude of the final R_I value. This is to date the only nitride material we have found to react so readily with air, and we are currently working on methods to further reduce the amount of air penetrating X-ray holders during diffraction. We are also in the process of preparing single crystals of Ba_2VN_3.

Initial cycles of the refinement included the variation of the scale factor, zero point, and lattice parameters. Atomic positions and peak width parameters were introduced as the refinement stabilized. As in Sr_2VN_3, variation of the isotropic temperature factors for the nitrogen atoms led to a destabilization in the refinement. The temperature factors of N2 and N3 were fixed without significantly reducing *R* factors. Impurity phases of Ba and BaO were simultaneously refined.

Results and Discussion

The final crystallographic results for Sr_2VN_3 and Ba_2VN_3 are shown in Tables 1 and 2. An observed, calculated, and difference plot for the refinements of Sr_2VN_3 is shown in Figure 1.

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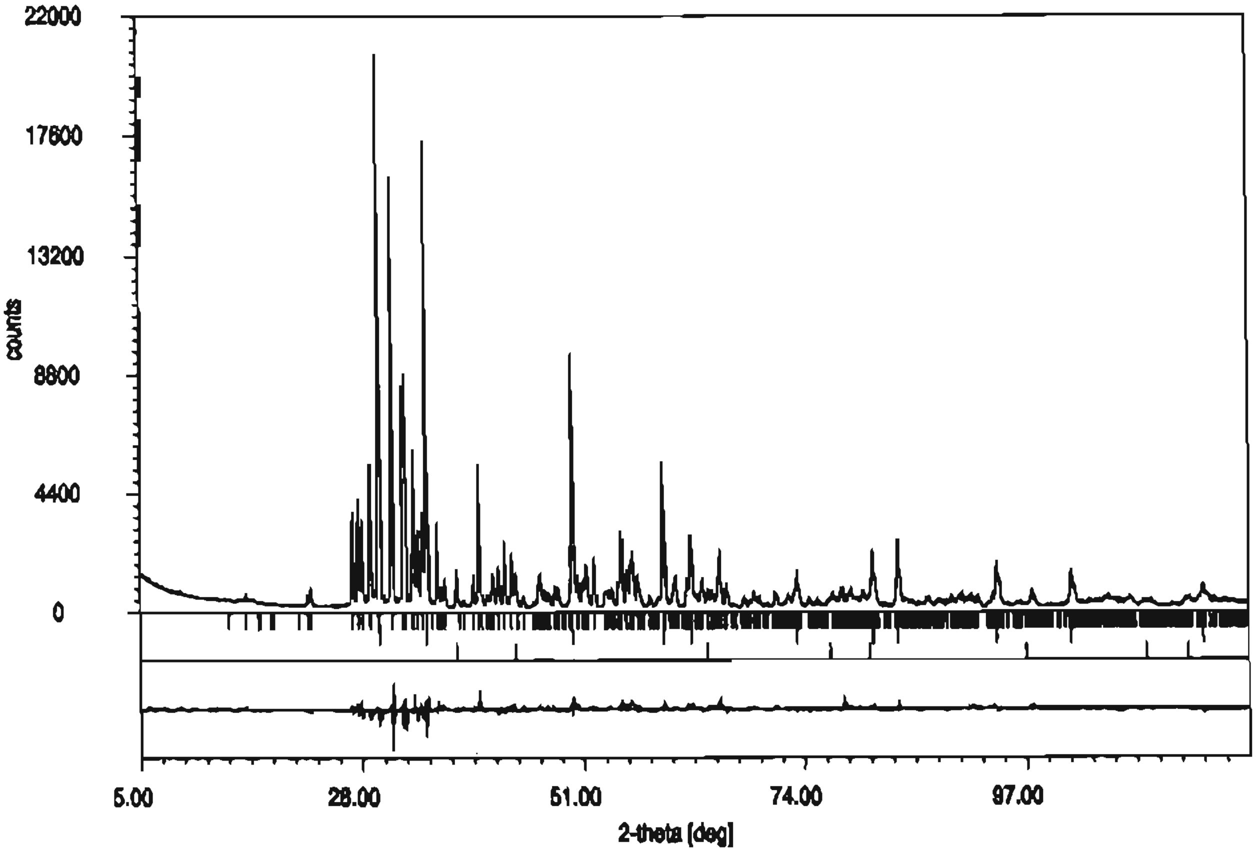

Figure 1. Observed, calculated, and difference plot for Sr_2VN_3.

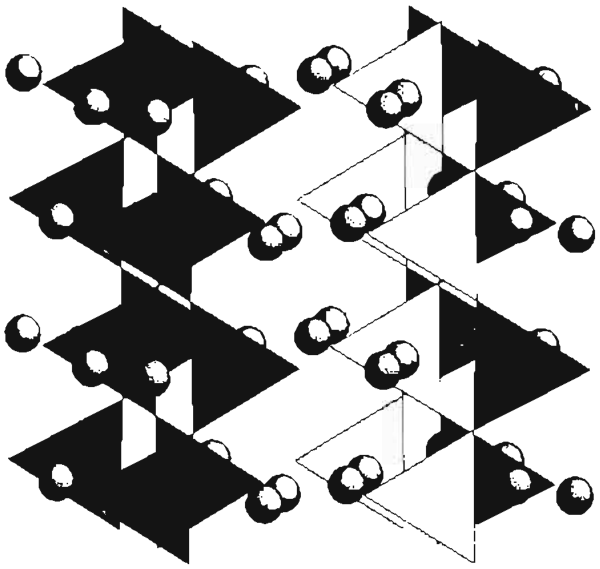

Figure 2. Structure of Sr_2VN_3 parallel to the 100 plane.

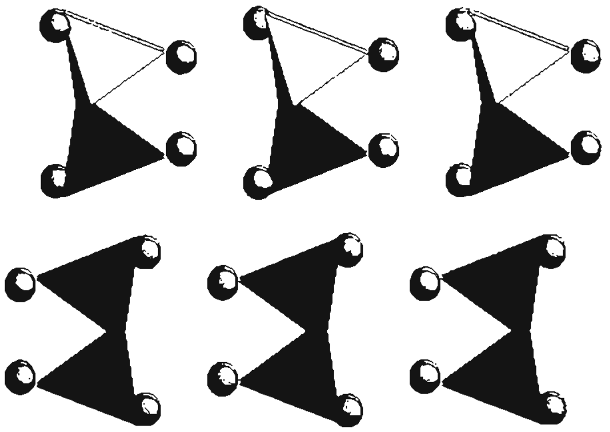

Figure 3. Structure of Sr_2VN_3 viewed down the 001 direction.

Table 3. Bond Lengths in Sr_2VN_3 (Å)

Sr1−N1	2.631(12)	Sr1−N4	2.710(12)
Sr1−N1	2.671(11)	Sr1−N4	2.749(14)
Sr1−N2	2.658(3)	Sr1−N4	3.018(14)
Sr1−N3	2.708(6)		
Sr2−N1	2.720(11)	Sr2−N3	3.054(13)
Sr2−N1	2.721(13)	Sr2−N4	2.586(12)
Sr2−N1	3.061(13)	Sr2−N4	2.654(11)
Sr2−N2	3.233(13)		
V−N1	1.763(13)	V−N3	1.841(4)
V−N2	1.875(7)	V−N4	1.760(11)

Sr_2VN_3 (Figures 2 and 3) has the Ba_2ZnO_3[13] structure, is isotypic with Sr_2TaN_3, Ba_2TaN_3,[14] and Ba_2NbN_3,[15] and consists of Sr^{2+} cations and nitridovanadate anions. Infinite chains of vertex-linked tetrahedral $[VN_3]^{4-}$ groups are arranged parallel to the [100] plane with a chain pattern that repeats after two tetrahedra. The monoclinic distortion is considerably smaller in Sr_2VN_3 than in the nitridotantalates[14] and than in Ba_2NbN_3.[15] Bond lengths and angles of interest in Sr_2VN_3 are shown in Tables 3 and 4.

The average V−N bond length in these $[VN_3]^{4-}$ units is 1.810(9) Å, and there are few nitride structures with which to compare this distance. It is, as expected, smaller than the equivalent mean Ta−N distance in Ba_2TaN_3[14] (1.957(8) Å) and the equivalent mean Nb−N distance in Ba_2NbN_3[15] (1.943(8) Å). Perhaps more surprisingly it is not appreciably different from that of the mean V(III)−N distance in the planar $[VN_3]^{6-}$ units found in Ca_3VN_3[5] (1.819(7) Å). The $[VN_3]^{4-}$ tetrahedra are somewhat distorted with two longer bridging V−N bonds of 1.875(7) and 1.841(4) Å connecting neighboring units along the chain and two essentially equal shorter "terminal" V−N

Table 4. $[VN_3]^{4-}$ Bond Angles in Sr_2VN_3 (deg)

N1−V−N4	115.7(5)	N2−V−N4	107.1(4)
N2−V−N3	101.8(3)	N3−V−N4	109.2(4)
N1−V−N2	112.3(4)	V−N2−V	137.7(1)
N1−V−N3	109.4(4)	V−N3−V	163.5(1)

Table 5. *Site Valences in* A_2MN_3 *Materials*

nitride	A1 site valence	A2 site valence	M site valence	ref
Ba_2TaN_3	2.1	1.7	4.6	14
Ba_2NbN_3	2.1	1.7	5.5	15
Sr_2VN_3	1.9	1.5	4.6	this work

distances of 1.763(13) and 1.760(11) Å. Neighboring $[VN_3]^{4-}$ tetrahedra are connected to one another through angles of 163.5(1)° (V−N3−V) and 137.7(1)° (V−N2−V). This arrangement is similar to that reported in the nitridotantalates[14] where in Ba_2TaN_3 neighboring tetrahedra are connected through angles of 170.8(8)° and 133.5(12)° and in Ba_2NbN_3[15] where the equivalent angles Nb1−N3−Nb2 and Nb1−N2−Nb2 are 173(1) and 129(1)°, respectively.

Each Sr atom is coordinated to seven nitrogen atoms with distances ranging from ~2.6 to ~3.2 Å. Sr1 is coordinated to nitrogen in a distorted 7-fold environment described as a distorted pentagonal bipyramid whereas Sr2 adopts a capped trigonal prismatic geometry. The average Sr−N bond length is 2.798(11) Å, which is longer than that reported in Sr_2N[27] (2.6118(3) Å) or in the 313 phases Sr_3MnN_3[6] (2.723(9) Å) and Sr_3CrN_3[28] (2.718 Å). The longer distances appear large for Sr−N bonds but are similar to those observed in $Sr_3Al_2N_4$[12] (2.508(7)−3.216(7) Å), where similar MN_4 tetrahedral units are observed, but in this instance the chains of Al−N tetrahedra are edge-connected.

Bond valence calculations have been used extensively in recent years in oxide systems to derive and confirm cationic oxidation states from experimentally observed bond lengths.[29] This has found a particular application in superconducting (and nonsuperconducting) cuprate systems, where the process of superconductivity is thought to depend significantly on the valence of the copper species. Bond length parameters were recently extended for systems containing anions other than oxygen by Brese and O'Keefe, allowing metal valences in nitride systems to be deduced from observed bond lengths.[30,31] The valence, v_{ij}, for a bond between atoms i and j is given by

$$v_{ij} = \exp[(R_{ij} - d_{ij})/b]$$

where R_{ij} is the bond valence parameter for a bond between i and j derived from observed experimental bond lengths and b is a universal constant (0.37 Å). The valence, V_i for atom i is thus the sum of these bond valences:

$$V_i = \sum_j v_{ij}$$

Using bond valence parameters, R_{ij}, for Sr−N and V−N of 2.23 and 1.86 Å respectively, the valences of the two cations in Sr_2VN_3 have been evaluated. Calculations yielded oxidation states of 1.9(1) for Sr1, 1.5(1) for Sr2, and 4.6(4) for V. The value for the Sr2 site valence is lower than expected whereas that for Sr1 is close to the expected +2 state. The value calculated for V is encouraging, confirming the likely oxidation state of +5.

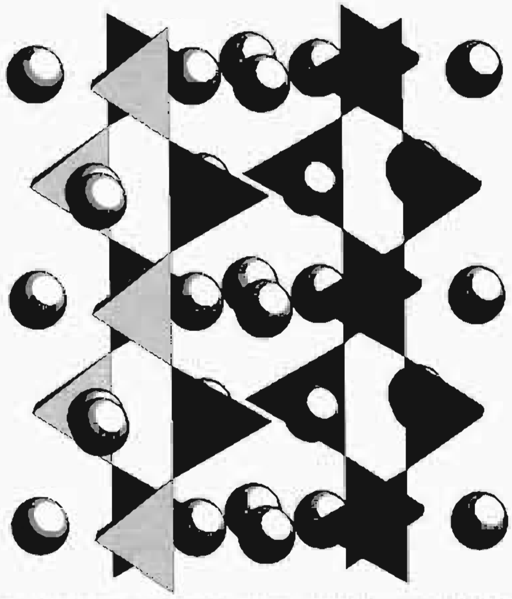

Figure 4. Structure of Ba_2VN_3 viewed parallel to the 100 plane.

It is interesting to compare these values with those calculated from bond lengths in other A_2MN_3 phases (Table 5). In all the nitride phases, the A1 site valence is effectively unchanged and is very close to the expected value of +2. The A2 site valence lies below +2 in each composition and is lowest in Sr_2VN_3. These A2 sites contain A^{2+} in cavities that are too large, and as the cation size decreases from Ba^{2+} to Sr^{2+}, so the site valence correspondingly decreases. One would perhaps expect the A_2MN_3 structure to become more distorted as the ion occupying the A2 site decreases in size. This appears to be the case in these materials where in A_2TaN_3[14] the monoclinic angle increases with decrease in cation size (A = Ba, $\beta = 91.1(1)°$; A = Sr, $\beta = 91.71(6)°$) and here in A_2VN_3 where the structure moves to lower symmetry as A^{2+} becomes smaller.

It is perhaps useful to compare the Sr site valences with those obtained for Sr in Sr_2N[27] In the binary nitride a site valence of only ~1.2 was obtained where it was suggested strontium could have a formal oxidation state of 1.5. The Sr2 site in Sr_2VN_3 has a similarly low valence, yet a formal oxidation state of 1.5 would tend to suggest an impossibly high vanadium valence or a nitrogen deficiency. Clearly the latter postulate cannot be accurately tested by X-ray diffraction.

The M site valences in the M = V, Ta materials are slightly lower than expected whereas in Ba_2NbN_3 the calculated Nb valence is above 5. This contrast between Nb and Ta is perhaps surprising, given the negligible difference in ionic radius.

Ba_2VN_3 has the Rb_2TiO_3[16] structure (Figure 4) and is not monoclinically distorted as is the Ba_2TaN_3[14] structure. Thus the monoclinic distortion is apparently reduced by increasing the size of A in these A_2VN_3 materials as suggested by bond valence calculations (Table 5 and above). In all other respects the structures are very similar. The arrangement of the A−N and V−N polyhedra is as observed in Sr_2VN_3 with infinite corner-connected chains of $[VN_3]^{4-}$ tetrahedra aligned parallel to the [100] direction with a chain pattern repeating after two tetrahedra. The $[VN_3]^{4-}$ tetrahedra appear less elongated than those in Sr_2VN_3, and here the orthorhombic symmetry forces equidistant "bridging" nitrogens (N3). Bond lengths and angles of interest in Ba_2VN_3 are shown in Tables 6 and 7.

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Table 6. Bond Lengths in Ba_2VN_3 (Å)

Ba1−N1 (×1)	2.50(3)	Ba1−N2 (×2)	2.961(5)
Ba1−N1 (×1)	2.86(3)	Ba1−N3 (×2)	3.16(2)
Ba1−N2 (×1)	2.85(4)		
Ba2−N1 (×2)	2.936(2)	Ba2−N2 (×1)	2.80(4)
Ba2−N1 (×1)	3.05(3)	Ba2−N3 (×2)	2.85(1)
Ba2−N2 (×1)	2.79(3)		
V−N1 (×1)	1.80(4)	V−N3 (×2)	1.859(9)
V−N2 (×1)	1.85(4)		

Table 7. $[VN_3]^{4-}$ Bond Angles in Ba_2VN_3 (deg)

N1−V−N2	122(1)	N3−V−N3	104.0(6)
N1−V−N3 (×2)	110.0(1)	V−N3−V	165.1(4)
N2−V−N3 (×2)	104.2(7)		

Given the presence of β-$Ba(OH)_2$ in the diffraction profile, the bond lengths and angles for Ba_2VN_3 are likely to be at best approximate. The average V−N bond length in Ba_2VN_3 is 1.84(2) Å, which is larger than that observed in Sr_2VN_3, although the error in this distance reflects the reliability of the finally refined structure. The refinement gives V−N bond lengths that are nearly equal with marginally longer V−N3 "bridging" bonds. This is analogous not only to the structures of other A_2MN_3 materials but also to those of isostrucutral Rb_2TiO_3[16] (Ti−O1 = 1.73 Å, Ti−O2 = 1.74 Å, Ti−O3 = 1.87 Å (×2)) and Cs_2CoO_3.[32] In these other nitrides and oxides, however, the contrast between "bridging" and "terminal" nitrogen or oxygen distances is more pronounced. The V−N tetrahedra are connected through an angle of 165.1(4)°, which is close to the V−N3−V angle in Sr_2VN_3. The tetrahedral angles are similar to those in Rb_2TiO_3 with one exception—the large N1−V−N2 angle 122(1)°, which contrasts with the much smaller analogous O1−Ti−O2 angle of 110.9°.

As in the monoclinic A_2MN_3 materials, Ba is coordinated to seven nitrogen atoms. In this material the Ba−N distances range from ~2.5 to ~3.2 Å, with an average Ba−N distance of 2.90(2) Å. This is smaller than the average Ba−N distances in the other reported Ba_2MN_3 phases[14,15] (M = Nb, Ba−N = 3.004(5) Å; M = Ta, Ba−N = 3.008 Å) but compares favorably with mean Ba−N bond lengths in other barium ternary nitrides such as Ba_3FeN_3[4] (Ba−N = 2.886(12) Å), Ba_3MnN_3[6] (Ba−N = 2.893(9) Å), $BaCeN_2$[33] (Ba−N = 2.88(1) Å), and BaCoN[34] (Ba−N = 2.860(12) Å). The Ba1−N1 distance of 2.50(3) Å in Ba_2VN_3 is very small for a barium−nitrogen bond length although Ba−N bond distances of ~2.6 Å have been reported in ternary nitrides such as Ba_3MoN_4, Ba_3WN_4,[35] and $Ba_8Ni_6N_7$.[36]

Bond valence analysis of the Ba and V sites in Ba_2VN_3 has been performed taking R_{ij} as 2.47 and 1.86 Å for Ba−N and V−N, respectively.[31] Site valences of 2.4(1), 2.3(1), and 4.2(3) were obtained for Ba1, Ba2, and V, respectively. Although the analysis can only be approximate, given the reliability of the data, certain inferences can be drawn. The Ba sites are close to the expected valence of +2 but are slightly high, probably implying some of the refined Ba−N distances are too short. It is difficult to correlate the cation size to the crystal symmetry on the basis of these calculations, but the A site valences may increase (and become close to 2) with increasing ionic radius, leading to a consequent decrease in the monoclinic angle, β (toward 90°). Accurate diffraction studies of Sr_2NbN_3 and Sr_2TaN_3 would probably help to clarify these structural relationships.

The V site valence is closer to 4 than the expected 5, and this would appear to be more a reflection of the refined V−N1 and V−N2 distances being too long rather than the presence of vanadium as V^{4+}.

In summary we have synthesized two new ternary nitride materials by the high-temperature reaction of the respective binary nitrides. Sr_2VN_3 is isostructural with the previously reported ternary materials Ba_2TaN_3, Sr_2TaN_3, and Ba_2NbN_3. Ba_2VN_3 represents a new structural type in ternary nitride chemistry and is isostructural with Rb_2TiO_3. These materials are the first reported group II ternary nitrides containing V^{5+}.

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Supporting Information Available: Lists of X-ray diffraction data for Sr_2VN_3 and Ba_2VN_3, including *d* spacings, observed and calculated intensities, and indexed reflections, the final cycles in the refinements of Sr_2VN_3 and Ba_2VN_3 showing final crystallographic parameters and esd's, and an observed, calculated, and difference plot for the refinement of Ba_2VN_3 (20 pages). Ordering information is given on any current masthead page.

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