Synthesis and Structure of Two New Layered Ternary Nitrides, $SrZrN_2$ and $SrHfN_2$

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Received June 26, 1996[⊗]

The new ternary nitrides $SrZrN_2$ and $SrHfN_2$ have been synthesized by the solid state reactions of Sr_2N with ZrN and HfN and characterized by powder X-ray diffraction. Both nitrides form structures in the hexagonal space group $R\bar{3}m$ ($SrZrN_2$, $a = 3.37302(5)$ Å, $c = 17.6756(3)$ Å, $Z = 3$; $SrHfN_2$, $a = 3.34481(3)$ Å, $c = 17.6779(2)$ Å, $Z = 3$) and are isostructural with α-$NaFeO_2$. The structures are constructed of alternating layers of strontium−nitrogen edge-sharing octahedra and either zirconium−nitrogen or hafnium−nitrogen edge-sharing octahedra stacked along the *c* axis. Alternatively, Sr^{2+} can be regarded as occupying octahedral holes between $Zr(Hf)N_2$ octahedral layers. The title nitrides are essentially diamagnetic at room temperature, consistent with the chemical composition. These compounds are the first alkaline earth ternary nitrides observed to have the α-$NaFeO_2$ layered structure.

Introduction

There has been much interest in the chemistry of the ternary and higher order transition metal nitrides. Many of these materials have been the subject of speculation regarding their physical properties and potential applications. Preparative routes to ternary nitrides are often practically difficult, and there is no question that this has previously limited work in this field. Several groups have reported new ternary nitride compounds that exhibit a wide range of diverse and often novel crystal structures.[1−4] In some of these structures, transition metal ions display unusual oxidation states and/or coordination to nitrogen which are often unique to ternary nitride chemistry. For example, the families of ternary phases A_3MN_3 (313)[5−8] (A = alkaline earth, M = V, Cr, Mn, Fe) and Ca_6MN_5 (615)[9,10] (M = Fe, Ga, Mn) 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. Other nitrides adopt structures seen in carbide and oxide chemistry. For instance, CaNiN has the YCoC structure containing Ni(I) in chains of linear Ni−N units that run perpendicular to the long *c* axis.[11] Ba_2VN_3, however, forms the orthorhombic Rb_2TiO_3 structure containing chains of corner-sharing $[VN_3]^{4-}$ tetrahedra.[12]

Ternary nitrides of stoichiometry AMN_2 (A = alkali metal, alkaline earth metal, or transition metal; M = transition metal or lanthanide) crystallize in a variety of different structures. This stoichiometry is relatively well-documented for ternary alkali metal nitrides, and the majority of group 1a transition metal nitrides form layered structures similar to those seen in ternary oxide and chalcogenide chemistry. $LiMN_2$ (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 β-cristobalite whereas the ternary nitrides $NaMN_2$ (M = Nb, Ta) have the layered α-$NaFeO_2$ structure.[15−17] In the latter materials both cations are coordinated to nitrogen in an octahedral geometry.

Mixed transition metal nitrides such as $MnWN_2$, $CoWN_2$, $NiWN_2$,[18,19] $Fe_{0.8}Mo_{1.2}N_2$,[20] and $FeWN_2$[21] 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. $CuTaN_2$, however, crystallizes in the α-$CuFeO_2$-type (delafossite) structure.[22]

Alkaline earth ternary nitrides of the AMN_2 stoichiometry are much less well-known. Two structural types have been reported to date and these are also layered materials. $BaCeN_2$ is isostructural with β-$RbScO_2$ having Ce(IV) octahedrally coordinated to nitrogen and Ba^{2+} occupying trigonal prismatic holes.[23] Remaining known AMN_2 alkaline earth nitrides are formed with transition metals in group IVa. $SrTiN_2$ and $BaZrN_2$ are isostrucutral and form materials isotypic with $KCoO_2$ in which the layers consist of edge-sharing Ti−N or Zr−N square-based pyramids.[24,25] The alkaline earth ions in these compounds

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

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S0020-1669(96)00764-1 CCC: $12.00

are situated between M−N layers level with the apices of the pyramids. Magnetic measurements have been performed on the latter material. Given the nominal stoichiometry, $BaZrN_2$ shows anomalous magnetic behavior, exhibiting temperature-independent paramagnetism between 20 and 300 K.

As part of comprehensive research into the synthesis, crystal chemistry, and physical properties of ternary transition metal nitrides, we report here the syntheses and structures of two new layered AMN_2 materials, $SrZrN_2$ and $SrHfN_2$. These compounds are the first examples of alkaline earth metal nitrides with the α-$NaFeO_2$ structure, a structure commonly observed in AMO_2 materials.

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 as detailed in the preparation of other ternary strontium nitride phases.[8,12] 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 made 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 $SrZrN_2$ and $SrHfN_2$. Polycrystalline samples of $SrZrN_2$ and $SrHfN_2$ were prepared by the high-temperature solid state reaction of the binary alkaline earth nitride and either zirconium nitride (ZrN) (99%) or hafnium nitride (HfN) (99%) powders. All preparations were carried out in a purified argon-filled glovebox. The Sr_2N and ZrN (HfN) powders were thoroughly mixed, ground together in a 1:1 molar ratio, and pelleted using a hand press. The pellets were wrapped in a molybdenum foil tube and placed within stainless steel crucibles which were subsequently welded closed under purified argon. The stainless steel crucibles were fired in a tube furnace at 1000 °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 surfaces of the cooled crucibles were mechanically cleaned to remove any oxidized steel. The cleaned crucibles were then cut open in a nitrogen-filled glovebox. There was no apparent reaction of the nitrides with the Mo tube, and the resulting powders of $SrZrN_2$ and $SrHfN_2$ were both dark gray/green.

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 in a nitrogen-filled glovebox onto an aluminum slide contained in an aluminum holder with a Mylar film window and threaded removable cover with 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 $SrZrN_2$ and $SrHfN_2$ were shown to contain small amounts of SrO and Sr metal. These impurities are to be expected from the starting ratios which generate Sr as an additional product. Each sample also contained small quantities of the respective group IVa binary nitride, ZrN or HfN. 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 $R\bar{3}m$ by considering the observed reflections and systematic absences. A starting model was obtained by taking the well-documented α-$NaFeO_2$ structure and substituting Sr, Zr (Hf), and N for Na, Fe-, and O, respectively. A simulated powder pattern was generated using LAZY PULVERIX.[30] on a PC using the above model and the refined lattice parameters from the PXD data. A convincing agreement between the calculated and observed patterns was obtained. Diffraction data suitable for Rietveld refinement were collected over the range 5−130° 2θ with step size 0.02° 2θ. Scans were run for approximately 16 h. Full profile Rietveld refinements[31] of $SrZrN_2$ and $SrHfN_2$ were performed using the Philips PC RIETVELD PLUS[32,33] package with the above α-$NaFeO_2$-type structures as initial models 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 refined as a polynomial function in each case.

Initial cycles in the refinements of $SrZrN_2$ and $SrHfN_2$ allowed for the variation of the scale factor, zero point, background parameters, 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 without a destabilization in the refinement. Variation of the N site isotropic temperature factor in the refinement of $SrHfN_2$ led to a consistent small negative value being observed. In final cycles this was set to a low positive value, similar in magnitude to the metal site temperature factors, without increasing *R* factors.

Taking into account the anomalous magnetic behavior observed in $BaZrN_2$ and any possible associated nitrogen nonstoichiometry, variation of the occupancy of the N site was attempted during the refinements of the two strontium nitrides. However, in both cases, varying the N site occupancy led to values above 100%, a corresponding decrease of the isotropic temperature factor, and destabilization of the refinement. The N site occupancy was therefore left fixed at 100%. This is essentially consistent with the observed magnetic data (see below). It is not uncommon for layered AMX_2 phases to exhibit metal site disordering (for example, $LiMoN_2$ in ternary nitride chemistry[13]), especially when the sizes of A and M are similar. Although, Sr is somewhat larger than Zr or Hf (1.16, 0.72, and 0.71 Å for Sr^{2+}, Zr^{4+}, and Hf^{4+}, respectively, in 6-fold coordination),[34] the possibility was tested in the refinements of the two nitrides. Variation of the site occupancies indicated only a negligible degree of disorder with no decrease in *R* factors and a decrease in temperature factors to the point where either or both of the metal site *B* values fluctuated just above and below zero. The original ordered arrangement was thus retained in the final model.

Impurity phases of SrO, Sr, α-Sr, and ZrN (HfN) were simultaneously refined in each case. Quantitative analysis of the diffraction data running as part of the PC RIETVELD PLUS package yielded weight percentage values of 5.6% SrO, 5.5% Sr, 11.1% α-Sr, and 7.2% ZrN for $SrZrN_2$ and 14.0% SrO, 2.1% Sr, 4.1% α-Sr, and 2.6% HfN for $SrHfN_2$, respectively. Observed, calculated, and difference plots for the refinements of $SrZrN_2$ and $SrHfN_2$ are shown in Figures 1 and 2.

Magnetic Measurements. Magnetic susceptibility measurements were performed at room temperature using a Johnson Matthey magnetic susceptibility balance. Samples (ca. 0.15 g) of $SrZrN_2$ and $SrHfN_2$ were thoroughly ground and loaded into preweighed silica sample tubes in an argon-filled glovebox. Sample tubes were filled to a height of ca. 1.5 cm and sealed. After correction for the diamagnetism of the sample tubes, values for the total mass susceptibility, χ_g, of 3.393×10^{-6} and 1.705×10^{-7} emu g^{-1} were obtained for $SrZrN_2$ and $SrHfN_2$, respectively. The magnetic susceptibilities would appear to suggest intrinsically diamagnetic materials with varying amounts of paramagnetic impurities (either ZrN or HfN, for example) present in each sample.

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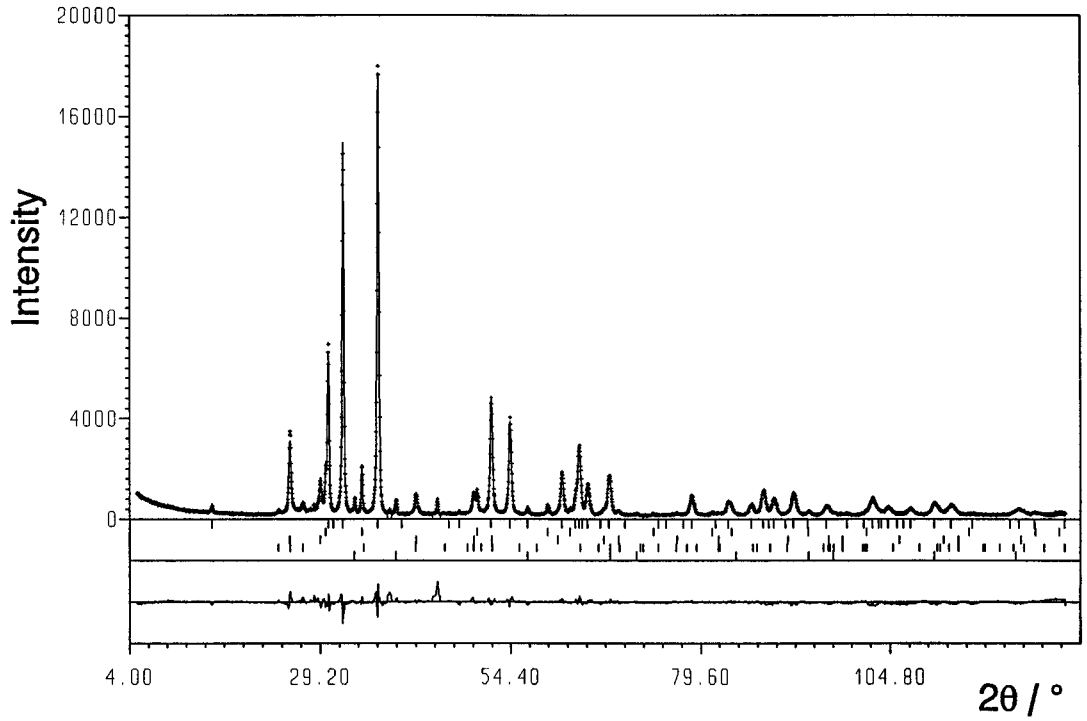

Figure 1. Observed, calculated, and difference plots for $SrZrN_2$.

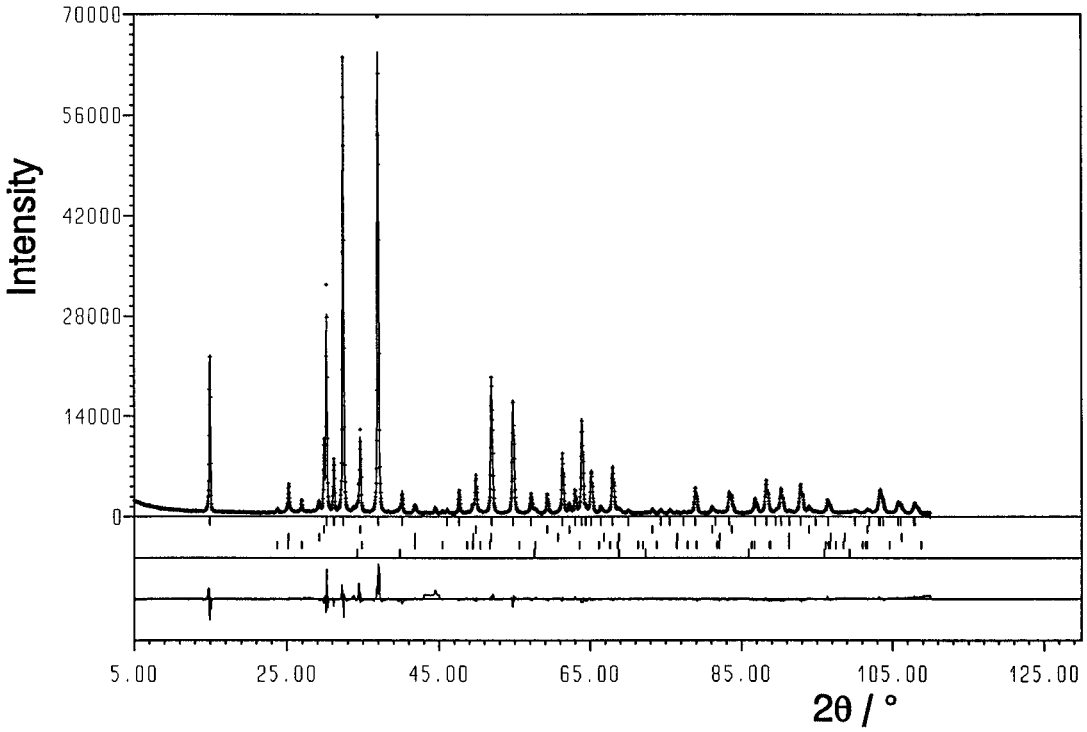

Figure 2. Observed, calculated, and difference plots for $SrHfN_2$.

Results and Discussion

The final crystallographic results for $SrZrN_2$ and $SrHfN_2$ are shown in Table 1. $SrZrN_2$ and $SrHfN_2$ are isostructural with each other and are isotypic with α-$NaFeO_2$. The structure is made up of $[ZrN_2]^{2-}$ or $[HfN_2]^{2-}$ anions and Sr^{2+} cations and is a rhombohedral distortion of the NaCl structure type brought about by the ordering of the A and M cations. The octahedral $[MN_2]^{2-}$ (M = Zr, Hf) anions are linked by edges in the *ab* plane to form layers separated by Sr^{2+} cations in octahedral holes (Figure 3). Thus alternating Zr (Hf)−N and Sr−N octahedral layers create infinite sheets stacked along the *c* axis. Sheet oxide materials can be classified according to their packing and cation coordination.[35] The zirconium and hafnium layered nitrides can be classified by analogy as so-called O3 structures where O refers to the octahedral coordination of the A cation and 3 refers to the number of $[MX_2]_n$ (X = O, S, or N in this instance) sheets present in the unit cell. The nitrogen layer packing follows a repeat pattern of ABCABC. Important interatomic distances and bond angles around the metal and nitrogen atoms in $SrZrN_2$ and $SrHfN_2$ are shown in Table 2.

The octahedral Zr−N and Hf−N anions are composed of the group IVa metals coordinated to six equidistant nitrogens at

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Table 1. Crystallographic Data for $SrZrN_2$ and $SrHfN_2$

	$SrZrN_2$	$SrHfN_2$
space group	$R\bar{3}m$	$R\bar{3}m$
a/Å	3.37302(5)	3.34481(3)
c/Å	17.6756(3)	17.6779(2)
atom (site)		
Sr (3a)		
x	0	0
y	0	0
z	0	0
B^a	0.33(4)	0.03(2)
Zr/Hf (3b)		
x	0	0
y	0	0
z	0.5	0.5
B^a	0.21(4)	0.05(2)
N (6c)		
x	0	0
y	0	0
z	0.2350(2)	0.2346(3)
B^a	0.24(9)	0.02
R_I/%	1.10	1.97
R_p/%	5.43	5.17
R_{wp}/%	7.38	7.64
R_e/%	1.41	0.78

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

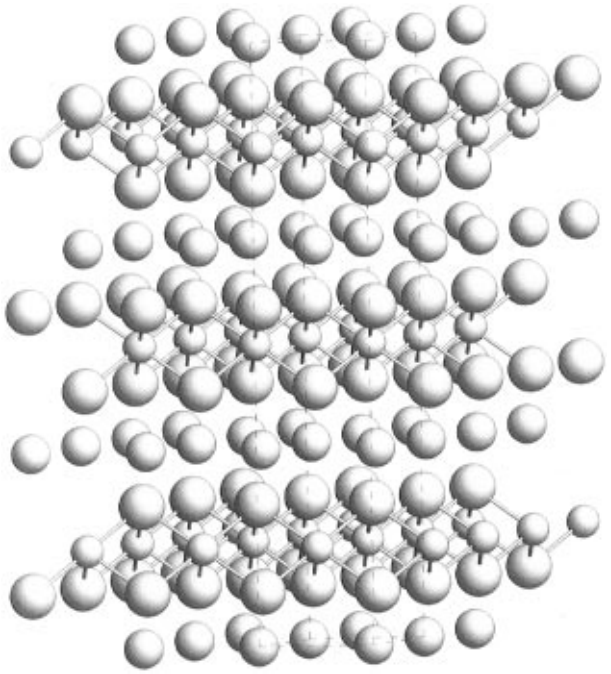

Figure 3. Structure of $SrZrN_2$ ($SrHfN_2$) viewed perpendicular to the long c axis. The unit cell is indicated by the dashed lines. Large spheres represent nitrogen atoms, medium spheres represent strontium atoms, and small spheres represent zirconium (hafnium) atoms.

2.292(2) and 2.273(2) Å for $SrZrN_2$ and $SrHfN_2$, respectively. There is some distortion with N−Zr(Hf)−N angles deviating significantly from 90° (six N−Zr(Hf)−N angles of ca. 95°, six N−Zr(Hf)−N angles of ca. 85°). As might be expected from the relatively small difference in ionic radius for Zr^{4+} and Hf^{4+} (0.72 and 0.71 Å, respectively[34]), there is no great disparity in the M−N bond lengths in the respective M−N anions. This is reflected in the overall structures where the a and c parameters are close in value and the cell volumes are very similar in size (∼174 and ∼171 $Å^3$ for $SrZrN_2$ and $SrHfN_2$, respectively).

The metal−nitrogen distances compare well to those seen in binary phases of zirconium and hafnium with nitrogen. The Zr−N distance in ZrN is 2.292(1) Å[36] whereas the mean Hf−N distances are 2.258 Å in Hf_3N_2 and 2.263 Å in Hf_4N_3.[37] The only reported ternary alkali metal or alkaline earth metal zirconium or hafnium nitrides are Li_2ZrN_2, Li_2HfN_2,[38−40] and $BaZrN_2$.[25] The lithium zirconium nitride was characterized recently by powder neutron diffraction.[40] Zirconium is coordinated to nitrogen in a regular octahedral geometry with a Zr−N bond distance of 2.253(2) Å. This distance is shorter than that observed in $SrZrN_2$. The mean Zr−N distance of 2.16(1) Å in $BaZrN_2$,[25] where Zr is in a square-based pyramidal coordination to N, is shorter still. The discrepancy in bond distances may be indicative of the degree of multiple Zr−N bonding in the nitrides but may also suggest a small degree of Sr/Zr disordering over the two metal sites in $SrZrN_2$.

Table 2. Selected Bond Lengths and Angles in $SrZrN_2$ and $SrHfN_2$

$SrZrN_2$

Sr−N/Å	N−Sr−N/deg	Sr−N−Sr/deg	Sr−N−Zr/deg
2.609(3) ×6	180.0(1) ×3	80.518(6) ×2	170.06(1) ×3
	99.48(8) ×6	80.514(6)	91.929(1) ×4
	80.52(8) ×6		91.935(1) ×2

Zr−N/Å	N−Zr−N/deg	Zr−N−Zr/deg
2.292(2) ×6	180.0(1) ×3	94.791(7) ×2
	94.79(9) ×4	94.785(7)
	94.78(9) ×2	
	85.20(9) ×4	
	85.21(9) ×2	

$SrHfN_2$

Sr−N/Å	N−Sr−N/deg	Sr−N−Sr/deg	Sr−N−Hf/deg
2.602(3) ×6	180.0(1) ×3	79.984(7) ×2	169.78(1) ×3
	100.01(9) ×4	79.980(7)	92.226(2) ×4
	100.02(9) ×2		92.231(2) ×2
	79.98(9) ×6		

Hf−N/Å	N−Hf−N/deg	Hf−N−Hf/deg
2.273(2) ×6	180.0(1) ×3	94.689(9) ×2
	94.7(1) ×6	94.682(9)
	85.3(1) ×6	

The nearly identical strontium−nitrogen distances in the compounds (2.609(3) and 2.602(3) Å in the zirconium and hafnium nitrides, respectively) are quite short when compared to those observed in other strontium ternary nitrides. Again, this may imply a low level of Sr/Zr(Hf) site disorder. Sr−N bond lengths are typically of the order of ∼2.7 Å in ternary nitrides. For example, mean Sr−N bond lengths of 2.723(9), 2.739(1), and 2.798(11) Å are found in Sr_3MnN_3,[6] Sr_3CrN_3,[8] and Sr_2VN_3,[12] respectively. The Sr−N distances in $SrZrN_2$ and $SrHfN_2$ are more on a par with the mean Sr−N distance observed in the binary nitride Sr_2N (2.6118(3) Å).[41]

It is worth noting at this point, however, the structural similarities between the two $SrMN_2$ (M = Zr, Hf) nitrides and Sr_2N. The latter has the *anti*-$CdCl_2$ structure. This is essentially an *anti*-α-$NaFeO_2$ structure with the (0, 0, $^1/_2$) (M) site vacant. Hence, although the N and Sr sites are interchanged in $SrMN_2$ (M = Zr, Hf) and Sr_2N, the Sr−N coordination environment is very similar. The octahedral arrangement of nitrogen around strontium in Sr_2N is also distorted in the equatorial plane, with supplementary Sr−N−Sr angles 84.83(2) and 95.17(2)°.[41] The equivalent N−Sr−N angles in $SrZrN_2$ and $SrHfN_2$ are ap-

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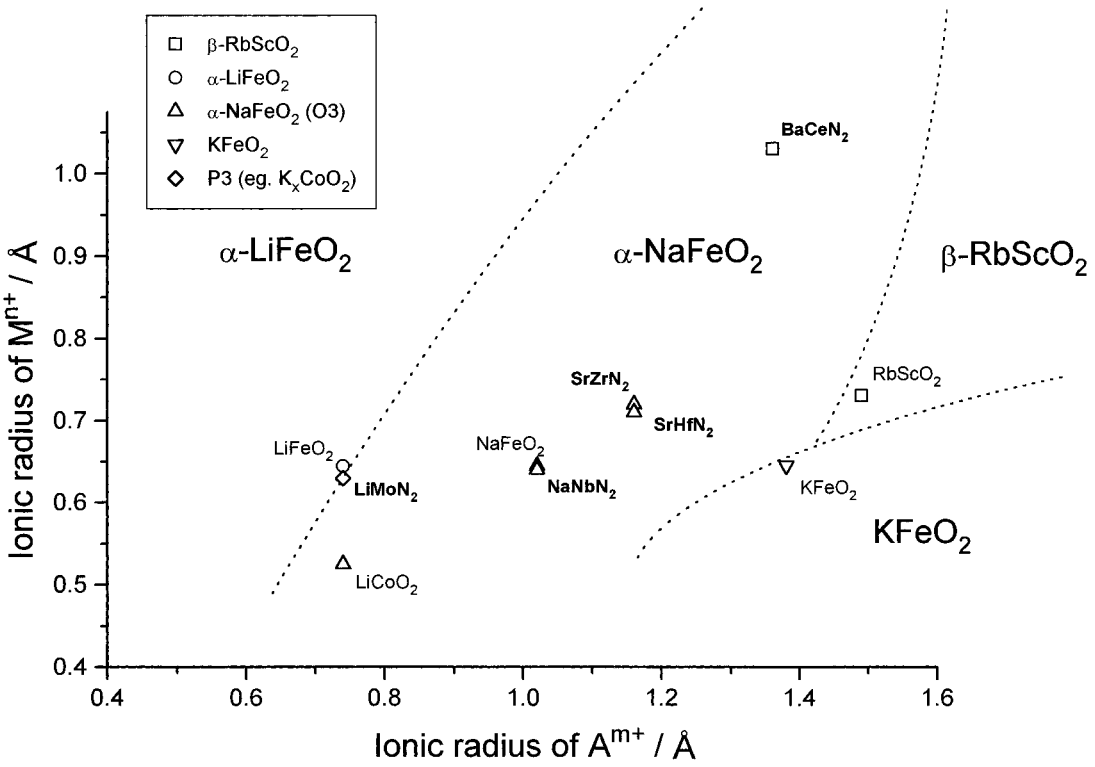

Figure 4. Plot of ionic radius of M against ionic radius of A in selected AMX_2 (X = O, N) compounds. Dashed lines show approximate phase boundaries according to ref 44. Ionic radii are taken from ref 34.

proximately 80 and 100°. This increased octahedral distortion, coupled with slightly shorter Sr−N bond lengths, leads to reduced (Sr−N) layer thicknesses in $SrZrN_2$ (∼2.41 Å) and $SrHfN_2$ (∼2.40 Å) compared to Sr_2N (2.73 Å). The interlayer distances in $SrZrN_2$ and $SrHfN_2$ are 3.476(6) and 3.489(11) Å. As might be expected, these distances are considerably shorter than the equivalent distance between N−Sr layers in Sr_2N (4.17 Å) reflecting the electrostatic repulsion between Sr layers in the latter material.

Nitrogen is coordinated to three strontium atoms and three zirconium (or hafnium) atoms in a distorted octahedral geometry. The octahedron is elongated toward the plane of three Sr atoms. The octahedron is "stretched" along *z* toward the Sr atoms (three Sr−N−Sr angles of ∼80.5°) and compressed along *z* in the direction of the Zr (Hf) atoms (three Zr−N−Zr angles of ∼94.8°).

Bond-valence calculations were performed for the two ternary nitrides using the bond-length parameters proposed by Brese and O'Keeffe for compounds with anions other than oxygen, fluorine, or chlorine.[42,43] The bond valence parameters used for Sr−N, Zr−N, and Hf−N were 2.23, 2.11, and 2.09 Å, respectively. The calculations resulted in Sr, M, N site valences of 2.15(2), 3.68(2), 2.92(2) and 2.19(2), 3.65(2), 2.93(2) in $SrZrN_2$ and $SrHfN_2$, respectively. The bonding environment changes little by replacing Zr^{4+} by Hf^{4+}, as might be expected from size arguments. In each case, the site valences for Zr or Hf and N are low whereas the site valence for Sr is high.

These results are unusual in the sense that alkaline earth metal valences are commonly lower than expected in binary and ternary nitrides whereas transition metal oxidation states are often higher than expected. Anomalous values for calculated valences are a reflection of shorter or longer than expected metal−nitrogen bonds or unexpected formal oxidation states. In the case of alkaline earth metals, it has been suggested that low values are a consequence of a lower oxidation state rather than longer than anticipated metal−nitrogen bond lengths. For example, in Sr_2N, the nominal stoichiometry implies an oxidation state of 1.5 and bond-valence calculations from neutron diffraction data yield a calculated valence of 1.224;[41] both values are well below the anticipated +2 state.

Conversely, transition metal valences are typically higher than expected in ternary nitrides as a result of shorter than anticipated bond distances. This is assumed to be a factor of multiple metal−nitrogen bonding. In these instances, the bond-valence parameters (which assume essentially ionic, or at least σ, bonds) are too large. For example, in the nitridochromates Ca_3CrN_3,[3] Sr_3CrN_3,[8] and Ba_3CrN_3,[8] the calculated chromium oxidation states are 3.47(7), 4.17(3), and 4.1(1), respectively.

That these trends are not observed in $SrZrN_2$ and $SrHfN_2$ perhaps suggests two things: first, that the transition metal−nitrogen bonding is essentially σ type (with bond lengths similar to those seen in the equivalent binary nitrides) and, second, that there is some degree of metal site disorder—consequently A−N bonds are on average shorter and M−N bonds are on average longer than might be envisaged. Bond-valence sums calculated from the crystallographic data for the other known ternary nitridozirconates indicate a varying degree of multiple Zr−N bonding. In $BaZrN_2$,[25] the Zr site valence is large, 4.4(1) as opposed to a value of 4.07(2) in Li_2ZrN_2.

The structures of the layered oxides, AMO_2, are well elucidated and have been characterized and classified in terms of ionic radii, interlayer separation, and ionicity.[35,44] As yet, the number of known AMN_2 ternary nitrides is comparatively small, but on the basis of ionic radii, some of the same general structural trends would seem to apply (Figure 4). For example, if the ionic radii of Sr^{2+}, Zr^{4+}, Hf^{4+} in a six-coordinate environment[34] are considered (assuming the relative values of the radii to be essentially unchanged in nitrides compared to oxides), $SrZrN_2$ and $SrHfN_2$ would be expected to lie in the

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α-$NaFeO_2$ region of the M^{n+} ($n = 3, 4, 5$) vs A^{m+} ($m = 1, 2$) graph. $NaNbN_2$, shown to crystallize with the α-$NaFeO_2$ (O3) structure,[17] would also lie in this region. $LiMoN_2$, however, which forms the P3 structure (where P denotes trigonal prismatic A coordination) adopted by nonstoichiometric phases such as K_xCoO_2 ($x < 1$), is placed just within the α-$LiFeO_2$ region close to the α-$NaFeO_2$ boundary. Similarly, $BaCeN_2$, with the β-$RbScO_2$ structure, is not situated within the β-$RbScO_2$ region as might be expected, but is found within the α-$NaFeO_2$ section of the graph. These inconsistencies perhaps highlight the differences in the nature of the bonding between some nitrides and oxides of the same stoichiometry. In this respect, a structure map taking into account metal−anion bond distances is probably more useful than one based purely on "ionic" radii.

The room-temperature magnetic susceptibility measurements carried out on samples of $SrZrN_2$ and $SrHfN_2$ are inconclusive. For materials of the nominal stoichiometry AMN_2 (where A is divalent), one would expect M to be in a +4 oxidation state. In the case of Zr^{4+} and Hf^{4+} (d^0, $s = 0$), one might also expect a diamagnetic response at room temperature. The presence of ZrN (ca. 8 wt %) and HfN (ca. 3 wt %) in the respective ternary nitrides clearly affects the magnetic measurements. Both of these binary nitride phases are paramagnetic at room temperature and superconducting at low temperature ($T_c = 10.0$ and 8.83 K, respectively).[45] For the ternary phases not to exhibit intrinsic diamagnetism, vacancies would have to be created in the lattice. Any extent of vacancies on the metal sites would lead to improbably high transition metal oxidation states. Reduction of the nitrogen site population would decrease the M valence (and increase the d electron configuration), but no evidence of this is seen in the structural refinement. Certainly, in oxide chemistry this structure type is most favorable when the A cation stoichiometry is close to 1 and no anion vacancies are observed. Furthermore, no cation or anion vacancies are observed in the structure of $NaNbN_2$.[17] However, powder X-ray diffraction is limited in its ability to accurately detect small vacancy levels of light elements, and we hope to be performing powder neutron diffraction experiments on the nitrides in the near future.

Acknowledgment. We thank the EPSRC for a postdoctoral fellowship (D.H.G.) and for financial support of this work.

Supporting Information Available: Listings of X-ray diffraction data, including *d* spacings, observed and calculated intensities, and indexed reflections, and the final cycles in the refinements of $SrZrN_2$ and $SrHfN_2$ showing final crystallographic parameters and esd's (24 pages). Ordering information is given on any current masthead page.

IC9607649

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