Synthesis and crystal structures of the new ternary nitrides Sr_3CrN_3 and Ba_3CrN_3

Marten G. Barker,[a] Michael J. Begley,[a] Peter P. Edwards,[b] Duncan H. Gregory[a] and Susan E. Smith[b]

[a] *Department of Chemistry, The University of Nottingham, Nottingham NG7 2RD, UK*
[b] *School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*

Two new ternary nitrides, Sr_3CrN_3 and Ba_3CrN_3, were synthesised from the appropriate alkaline-earth-metal nitride and chromium metal or the chromium nitride, Cr_2N, at high temperatures in sealed stainless-steel capsules. Structure determination from single-crystal X-ray data showed them to be isostructural in the hexagonal space group $P6_3/m$, $Z = 2$, with lattice constants $a = 7.724(2)$, $c = 5.249(1)$ Å for Sr_3CrN_3 and $a = 8.201(2)$, $c = 5.497(1)$ Å for Ba_3CrN_3. The structures contain trigonal-planar $[CrN_3]^{6-}$ anions and either Sr^{2+} or Ba^{2+} cations.

Whilst a very large number of ternary oxides have been prepared containing alkaline-earth and transition elements it is only in the past few years that the corresponding ternary nitride systems have begun to be investigated in detail. Even now a wide range of often novel structure types have been shown to exist in ternary nitrides. The valences and co-ordinations exhibited by transition metals in these materials can be unusual often leading to interesting physical properties.[1,2] Examples of such nitrides are the A_3MN_3 (313) (A = Ca, Sr or Ba; M = V, Cr, Mn or Fe)[3–7] and A_6MN_5 (615) (A = Ca; M = Ga, Fe or Mn)[8,9] series of materials. A particular feature of these compounds is the presence of a discrete $[MN_3]^{6-}$ anion possessing trigonal-planar co-ordination of M to nitrogen. In the strontium and barium compounds of manganese and iron, namely Sr_3MnN_3, Ba_3MnN_3[7] and Ba_3FeN_3,[6] the $[MN_3]^{6-}$ anion has D_{3h} symmetry, whilst in the corresponding calcium compounds of vanadium, chromium and manganese, Ca_3VN_3,[4] Ca_3CrN_3[3] and Ca_3MnN_3,[5] these anions have C_{2v} symmetry. In the case of the chromium nitride this change in symmetry was attributed to a Jahn–Teller instability for the low-spin Cr^{3+} ion.[3] Interestingly, the Ca_6MN_5 compounds appear to contain triangular units of D_{3h} symmetry[8,9] although magnetic measurements suggest there may be a local distortion of the anions.[9]

In this paper we report the first preparation and characterisation of two ternary nitrides, Sr_3CrN_3 and Ba_3CrN_3, which both contain the $[CrN_3]^{6-}$ anion having D_{3h} symmetry as opposed to the C_{2v} symmetry previously seen in Ca_3CrN_3.[3] We also outline the effects likely to govern the crystal structure and transition-metal co-ordination in A_3MN_3 materials in general and how these factors are likely to relate to their magnetic properties. With the crystal data now emerging, we can begin the task of establishing coherent structural correlations for these new materials.

Experimental

Starting materials

Strontium nitride was prepared by the reaction of strontium dissolved in liquid sodium with gaseous nitrogen at 570 °C. Previously cleaned strontium (2–3 g) was added to an excess of molten sodium contained in a stainless-steel crucible at 250 °C. This operation was carried out in an argon-filled, evacuable, glove-box specially designed for the handling of liquid alkali metals (*ca.* 5 ppm O_2, < 5 ppm water). On cooling, the crucible was sealed inside a stainless-steel vessel and heated to 570 °C for 42 h under a positive nitrogen pressure (*ca.* 2 atm, $\approx 2 \times 10^5$ Pa). During this time the nitrogen pressure was monitored continuously by a pressure transducer and further nitrogen added where necessary. When no further nitrogen was taken up by the alloy the vessel was cooled and then heated under vacuum at 350 °C for 24 h to remove the excess of sodium. Importantly, liquid sodium does not react with nitrogen and hence serves as an inert solvent for the strontium which reacts readily in this form with the nitrogen to give the binary nitride which precipitates from solution as a purple-black crystalline solid. This method of preparation was found to give a product free from alkaline-earth-metal oxide, an impurity which can sometimes be seen in nitride prepared by direct combination of the elements. X-Ray powder diffraction patterns of the resulting nitride showed it to be Sr_2N.[10] The chromium metal powder (99.95%), chromium nitride, Cr_2N (99%), and barium nitride, Ba_3N_2, used in this study were obtained commercially (Alfa).

Synthesis of Sr_3CrN_3 and Ba_3CrN_3

Single crystals of both compounds were prepared by the reaction of the binary nitrides with chromium metal powder (99.95%) in sealed stainless-steel crucibles at 1050 °C for a period of 4 d, after which the reaction mixture was cooled under argon at a rate not exceeding 20 °C h^{-1}. The latter conditions were essential for the formation of single crystals. Polycrystalline powder samples were obtained using a similar heating cycle starting with the binary nitride and chromium nitride (Cr_2N, 99%) powders. The high reactivity of the alkaline-earth-metal nitrides and the ternary nitrides towards water and oxygen necessitated that all manipulations of reaction mixtures and products be carried out in an argon-filled glove-box. The reagents were mixed in the appropriate molar ratios to yield the correct nominal nitrogen stoichiometry and compressed into pellets with a hand-press before being placed into stainless-steel crucibles which were then welded closed in an argon atmosphere. These crucibles were heated in a tube furnace under flowing argon to minimise external aerial oxidation at the high temperatures employed. The crucibles were cooled, cut open in the argon-filled glove-box and the reaction products removed. Single crystals of each nitride were green, needle-like and up to 0.5 mm in length. The corresponding polycrystalline products of each reaction were dark green powders.

Initial characterisation of polycrystalline products by powder X-ray diffraction [using a Philips X'PERT (1992) system] required the design and construction of a sample holder which protected the sample from the atmosphere (Fig. 1). This comprised an aluminium cylinder sectioned around part of its circumference to allow the passage of X-rays to the sample. The open area was sealed with Mylar film which is transparent to X-rays but is relatively impermeable to oxygen and moisture. The front of the cylinder was machined to take a removable cover and an 'O'-ring seal which allowed a standard sample mount to be loaded into the cylinder in the glove-box. The back face of the cylinder contained a plate which served precisely to locate the sample in its correct position relative to the centre of the diffractometer, also as a means of mounting the cylinder onto the diffractometer. Using this sample chamber, powder patterns of very air-sensitive materials can be recorded routinely without any extraneous diffraction peaks from the Mylar film.

X-Ray diffraction patterns of both Sr_3CrN_3 and Ba_3CrN_3 showed them to be isostructural and to index in the hexagonal space group $P6_3/m$. For all the preparations carried out the product was found (by Rietveld refinement using the PC-RIETVELD PLUS program[11–13]) to contain a small amount of alkaline-earth-metal oxide (*ca.* 10 wt%) and chromium metal (*ca.* 2 wt%). The presence of the oxide is probably due to the high reactivity of the binary nitrides towards oxygen particularly when finely ground, and the impurities therefore arise from the oxidation of unreacted starting materials.

Structure determinations

The unit-cell constants and space-group assignment were confirmed by oscillation and Weissenberg photographs taken of crystals sealed under argon in 0.2 mm diameter glass capillaries. It was found necessary carefully to degas the capillaries by heating for several hours under vacuum (*ca.* 1×10^{-5} Torr, *ca.* 1.33×10^{-3} Pa) prior to loading them in the glove-box. Green crystals of dimensions $0.28 \times 0.02 \times 0.03$ (Sr_3CrN_3) and $0.19 \times 0.02 \times 0.04$ mm (Ba_3CrN_3), sealed as above, were used in the structure determinations. Data were collected at 298 K on a Hilger and Watts Y290 four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å). The structures were solved by heavy-atom methods in the space group $P6_3/m$ (no. 176). The unit-cell dimensions were refined using 25 independent reflections in the range $15 < 2\theta < 25°$. The structure determinations and full-matrix least-squares refinements were carried out using the CRYSTALS program[14] and absorption corrections were made using the DIFABS routine.[15] The structures were solved using 456 and 460 reflections respectively for Sr_3CrN_3 and Ba_3CrN_3 with $F_o > 3\sigma(F_o)$. The function minimised in the least-squares refinements was $\Sigma w(|F_o| - |F_c|)^2$ with $w = \sigma^{-2}$. Anisotropic refinements of all atoms converged to $R = 0.0192$, $R' = 0.0189$ for Sr_3CrN_3 and $R = 0.0347$, $R' = 0.0395$ for Ba_3CrN_3. The data collection parameters are summarised in Table 1 and atomic positions are given in Table 2.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

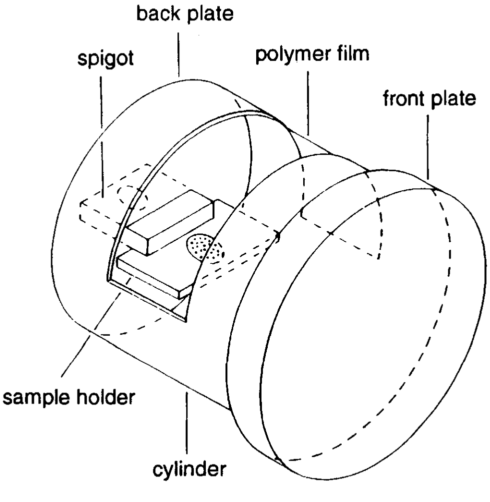

Fig. 1 Schematic representation of powder X-ray diffraction holder used for air-sensitive samples

Results and Discussion

The unit cells of both compounds contain two planar triangular $[MN_3]^{6-}$ anions and six alkaline-earth-metal cations. The compounds are isostructural with Ba_3FeN_3[6] consisting of either Sr^{2+} or Ba^{2+} cations and discrete $[MN_3]^{6-}$ units of D_{3h} symmetry in contrast to the situation in Ca_3CrN_3[3] in which the $[MN_3]^{6-}$ units have C_{2v} symmetry (Fig. 2). In the unit cell neighbouring $[MN_3]^{6-}$ units are displaced by $\frac{1}{2}$ in z and the orientation of the triangle is reversed. The stacking of the layers in these nitrides thus follows the sequence [$\cdots$ABAB$\cdots$] along the [001] direction (Fig. 3). A selection of bond lengths and angles for both ternary nitrides is given in Table 3.

The three equivalent metal–nitrogen bond lengths within each $[MN_3]^{6-}$ unit are almost identical, being 1.728(3) Å in Sr_3CrN_3 and 1.732(8) Å in Ba_3CrN_3. These values are slightly reduced as compared to the two shorter Cr–N distances observed earlier in the $[MN_3]^{6-}$ unit in Ca_3CrN_3 [1.766(7) Å] and more significantly lower than the mean Cr–N distance [1.799(7) Å] in the calcium material.[3] The distances in the strontium and barium 313 materials are also smaller than those reported in the lithium ternary nitride $Li_{15}Cr_2N_9$ [1.760(8) and 1.780(8) Å] and the oxide nitride $Li_{14}Cr_2N_8O$ [1.749(5) and 1.767(6) Å].[16] The recently reported barium–chromium phase, Ba_5CrN_5,[17] with Cr^V in tetrahedral co-ordination to N, also has two Cr–N distances [1.753(4) and 1.758(5) Å] slightly longer than those seen in the barium 313 composition. All of these bond distances suggest that the metal–nitrogen bonds in these compounds are multiple since Cr–N single bonds are considered to lie in the range ≈2.00–2.25 Å[18] in molecular solids

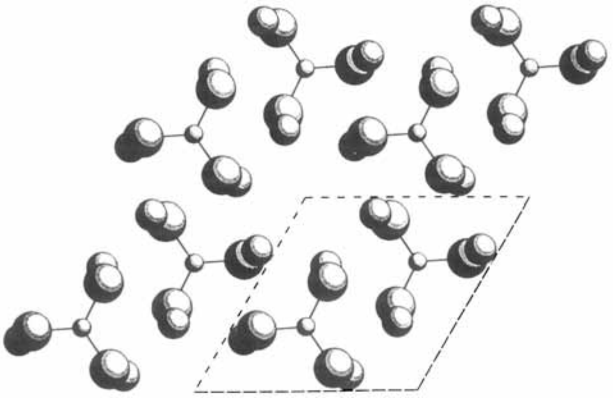

Fig. 2 Structure of Sr_3CrN_3 viewed as a projection on the *ab* plane. The unit cell is indicated by dashed lines. Small spheres represent Cr, medium spheres Sr and large spheres N

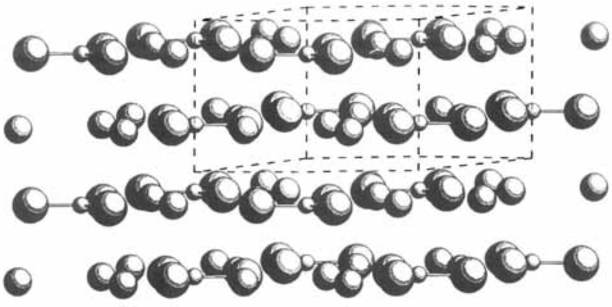

Fig. 3 Structure of Sr_3CrN_3 illustrating the packing of the layers along the *c* axis. The unit cell is indicated by dashed lines. Key as in Fig. 2

Table 1 Diffraction data for Sr_3CrN_3 and Ba_3CrN_3 [a]

	Sr_3CrN_3	Ba_3CrN_3
a, c/Å	7.724(2), 5.249(1)	8.201(2), 5.497(1)
U/Å^3	271.2(2)	320.2(2)
D_c/g cm^{-3}	4.368(2)	5.247(3)
μ/cm^{-1}	302.4411	197.2422
Measured reflections	821	1053
Observed reflections [b]	456	460
Independent reflections	192	243
F(000)	318	426
Largest difference peak/e Å^{-3}	0.823	1.32
R,[c] R'[d]	1.92, 1.89	3.47, 3.95

[a] Details in common: hexagonal, space group $P6_3/m$; $Z = 2$; $2\theta_{max}$ 55°; ω–2θ scans; octants collected ±hkl; parameters 15. [b] $F_o > 3\sigma(F_o)$. [c] $\Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$. [d] $\{\Sigma[w(|F_o| - |F_c|)^2]/\Sigma(w|F_o|^2)\}^{\frac{1}{2}}$, $w = \sigma(F_o)^{-2}$.

Table 2 Positional parameters for Sr_3CrN_3 and Ba_3CrN_3

Atom (site)		Sr_3CrN_3	Ba_3CrN_3
Sr/Ba (6h)			
	x	0.354 55(6)	0.358 91(8)
	y	0.268 93(7)	0.273 89(7)
	z	0.25	0.25
Cr (2d)			
	x	0.666 67	0.666 67
	y	0.333 33	0.333 33
	z	0.75	0.75
N (6h)			
	x	0.434 7(5)	0.447 7(12)
	y	0.315 8(5)	0.317 1(11)
	z	0.75	0.75

Table 3 Selected bond lengths and angles in Sr_3CrN_3 and Ba_3CrN_3

Sr–N/Å	N–Sr–N/°	Sr–N–Sr/°	Sr–N–Cr/°
2.6793(7) × 2	156.8(1)	156.8(1)	99.85(7)
2.699(3)	95.79(6) × 2	84.25(7) × 2	88.1(1)
2.778(3)	83.19(7) × 2	96.81(7) × 2	85.6(1)
2.858(3)	92.16(6) × 2	81.24(7) × 2	170.9(2)
	66.2(1)	173.8(1)	
	139.07(11)	100.9(1)	
	154.70(8)	85.30(8)	
Cr–N	N–Cr–N		
1.728(3) × 3	120 × 3		
Ba–N/Å	N–Ba–N/°	Ba–N–Ba/°	Ba–N–Cr/°
2.820(2) × 2	154.1(3)	154.1(3)	101.7(1) × 2
2.866(8)	97.4(1) × 2	84.6(2) × 2	89.3(3)
2.905(8)	84.1(2) × 2	95.9(2) × 2	88.0(3)
3.160(7)	91.0(1) × 2	79.4(1) × 2	170.8(4)
	62.6(3)	177.4(3)	
	140.2(2)	99.8(2)	
	157.2(2)	82.8(2)	
Cr–N/Å	N–Cr–N/°		
1.732(8) × 3	120 × 3		

whilst the Cr–N triple bond is 1.57 Å[19] (note also Cr–N distances of 1.929 and 1.936 Å in Cr_2N[20] and 2.070 Å in CrN[21]). The triangular units in the strontium and barium 313 compounds are separated along z by a layer of three cations which gives a large metal–metal separation of 5.250 Å in the strontium compound and 5.475 Å in the barium compound. Both of these distances are considerably longer than the equivalent shortest Cr⋯Cr distance of 4.726 Å observed in Ca_3CrN_3.[3]

Strontium and barium are five-co-ordinate to nitrogen in the respective compounds with the alkaline-earth-metal cation in a distorted trigonal-bipyramidal geometry. Conversely nitrogen is at the centre of a distorted octahedron with alkaline-earth-metal cations at the axial and three of the four equatorial positions and chromium at the remaining position. The alkaline-earth-metal–nitrogen bond distances compare well with those observed in the previously reported strontium and barium 313 materials. For example, Sr–N distances of between 2.649(13) and 2.797(9) Å are reported in Sr_3MnN_3 and Ba–N distances of between 2.835(12) and 3.209(9) are reported in Ba_3MnN_3.[7] The Sr–N distances in Sr_3CrN_3 are somewhat longer than those observed in the binary nitride, Sr_2N, where the Sr–N distance is 2.6118(3) Å (×6)[10] as compared to the mean distance in Sr_3CrN_3 of 2.739(1) Å. This is commonly the case for alkaline-earth-metal–nitrogen distances in ternary and binary nitrides. A comparison of the Ba–N distance in the ternary and binary nitrides cannot be made at this point since the crystal structure of Ba_3N_2 is as yet unknown.

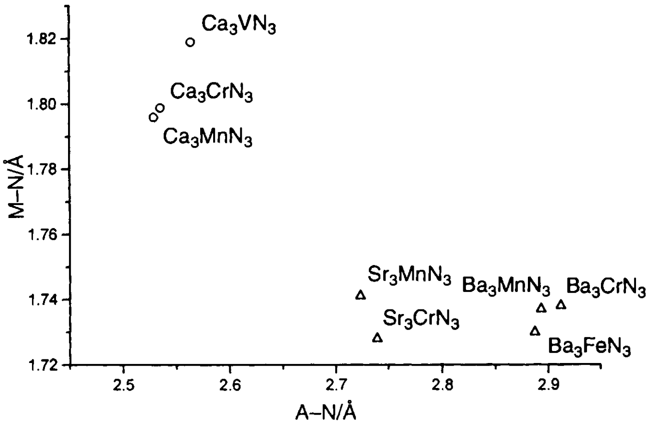

Fig. 4 Plot of transition metal–nitrogen bond length, M–N, against alkaline-earth-metal–nitrogen bond length, A–N, demonstrating the two structural regions of the 313 nitrides [orthorhombic, $Cmcm$, with $[MN_3]^{6-}$ units of C_{2v} symmetry (circles) and hexagonal, $P6_3/m$, with $[MN_3]^{6-}$ units of D_{3h} symmetry (triangles)]

Mean alkaline-earth-metal–nitrogen and transition metal–nitrogen bond lengths for 313 and 615 materials are shown in Table 4 together with the resulting M–N:A–N ratio for each composition. Table 4 is divided into three clear regions for the 313 nitrides: calcium nitrides with the smallest A–N distances, the largest M–N distances and the smallest M–N:A–N ratio (≈0.7); strontium nitrides with medium A–N distances, smaller M–N distances and a ratio of ≈0.63; barium nitrides with larger A–N distances, similar smaller M–N distances to those of the strontium materials and similar ratios to those of the strontium materials (≈0.6). It is worth noting that the M–N bond lengths do not effectively change with M across the period for any given A (this may also be true for the 615 materials where M is a transition metal). Furthermore, the M–N distances are unchanged in all the hexagonal 313 materials even when Sr is replaced by the larger Ba. By reducing the size of the alkaline-earth-metal cation sufficiently (for example from Sr to Ca) the hexagonal structure undergoes a monoclinic distortion to give the lower-symmetry structure. The two 313 structure types, orthorhombic and hexagonal, can, therefore, be tentatively defined in terms of the M–N:A–N ratios (Fig. 4).

The tendency of the 313 materials to form one or other of the two structural types would appear to have implications regarding the symmetry of the $[MN_3]^{6-}$ unit. It was suggested that the C_{2v} symmetry exhibited by the $[CrN_3]^{6-}$ unit in Ca_3CrN_3 was due to a Jahn–Teller distortion of the low-spin ($S = \frac{1}{2}$) d^3 Cr^{3+} ion in a trigonal-planar (D_{3h}) environment.[3] The d^2 V^{3+} ion, however, also formed a triangle with C_{2v} symmetry and was shown to be diamagnetic.[4] Later studies showed Mn^{3+} to form a similar $[MN_3]^{6-}$ unit.[5] Jahn–Teller distortion would clearly depend on the spin states of the transition-metal ions and calculations have shown that the most stable configurations for the $[MN_3]^{6-}$ anions arise when M is low spin.[22] The crystallographic data herein have shown that the equivalent strontium–barium-chromium 313 phases do not show any evidence of Jahn-Teller distortion at ambient

Table 4 Average bond lengths and A–N : M–N ratios in 313 and 615 materials

Nitride	Av. A–N/Å	Av. M–N/Å	M–N : A–N	Space group	Ref.
Ca_3VN_3	2.564	1.819(6)	0.709(2)	*Cmcm*	4
Ca_3CrN_3	2.535(5)	1.799(7)	0.710(3)	*Cmcm*	3
Ca_3MnN_3	2.529(2)	1.796(4)	0.710(2)	*Cmcm*	5
Sr_3CrN_3	2.739(1)	1.728(3)	0.631(1)	$P6_3/m$	This work
Sr_3MnN_3	2.723(8)	1.741(13)	0.639(7)	$P6_3/m$	7
Ba_3CrN_3	2.914(5)	1.732(8)	0.594(4)	$P6_3/m$	This work
Ba_3MnN_3	2.893(9)	1.737(12)	0.600(6)	$P6_3/m$	7
Ba_3FeN_3	2.887(12)	1.730(12)	0.599(7)	$P6_3/m$	6
Ca_6GaN_5	2.56(1)	1.951(28)	0.76(1)	$P6_3/mcm$	8
Ca_6MnN_5	2.569(2)	1.757(4)	0.683(3)	$P6_3/mcm$	9
Ca_6FeN_5	2.56(2)	1.770(15)	0.69(1)	$P6_3/mcm$	8

Table 5 Site valences derived from bond-valence calculations for 313 and 615 phases

	Site valence			
Nitride	A	M	N	Ref.
Ca_3VN_3	1.64, 1.65	3.35(6)	3.09, 2.64	4
Ca_3CrN_3	2.16(2), 2.20(2)	3.47(7)	3.13(5), 2.75(2)	3
Ca_3MnN_3	1.83(1), 1.779(8)	3.67(5)	2.92(3), 2.83(4)	5
Sr_3CrN_3	1.29(2)	4.17(3)	2.68(2)	This work
Sr_3MnN_3	1.33(3)	4.2(1)	2.75(8)	7
Ba_3CrN_3	1.58(6)	4.1(1)	2.96(5)	This work
Ba_3MnN_3	1.61(3)	4.3(1)	3.05(8)	7
Ba_3FeN_3	1.6(4)	4.2(1)	3.1(1)	6
Ca_6GaN_5	1.84(7)	2.2(2)	2.85(3), 2.5(1)	8
Ca_6MnN_5	1.69(1)	4.1(1)	2.94(1), 2.78(3)	9
Ca_6FeN_5	1.68(4)	4.1(4)	2.87(2), 2.7(1)	8

temperature. These nitrides form identical $[MN_3]^{6-}$ units to those seen in the other strontium and barium materials, Ba_3FeN_3,[6] Sr_3MnN_3 and Ba_3MnN_3.[7] It would appear that the symmetry of the trigonal-planar unit is therefore more dependent on the size of the alkaline-earth-metal cation (and hence the crystal symmetry) than on the d-electron configuration of the transition-metal ion.

Bond-valence calculations[23] have been performed for both of the A_3CrN_3 compounds using the bond-length parameters derived by Brese and O'Keeffe[24,25] for materials containing anions other than oxygen, fluorine and chlorine. The bond-valence parameters, R_{ij}, taken for Ba–N, Sr–N and Cr–N were 2.47, 2.23 and 1.85 Å respectively. Calculations yielded site valences of 1.29(2) and 4.17(3) for Sr and Cr in Sr_3CrN_3 and 1.58(6) and 4.1(1) for Ba and Cr in Ba_3CrN_3. Similar calculations have been performed for all previously reported 313 and 615 compositions and these are shown in Table 5. The site valences calculated for the strontium- and barium–chromium 313 phases are in close agreement with other 313 phases containing barium or strontium. All the 313 materials have consistently low alkaline-earth-metal site valences and consistently high transition-metal site valences. The values deviate significantly from the expected oxidation states in the A_3MN_3 hexagonal materials (A = Sr or Ba). The uniformly high transition-metal oxidation states are undoubtedly a reflection of multiple M–N bonds, covalent in nature. The values may also reflect some degree of compression in the M–N sublattice. The A site valences range from ≈ 1.3 to ≈ 2.2 but are closest to the expected valence of 2 in the calcium compounds and nearer 1.5 in those of Sr and Ba. This may suggest an 'overstretching' of the A–N sublattice or a lower formal oxidation state for A as suggested for Sr_2N where bond-valence calculations led to a similarly low value.[10] Transition-metal valences are highest in the hexagonal 313 materials and lie invariably closer to 4 than 3 whereas the opposite is the case for the orthorombic calcium compounds. No magnetic measurements have to date been performed on any of the hexagonal nitrides of Sr or Ba. It will be interesting to see what spin states are inferred for the transition-metal ions in these compounds. It is worth noting that the M site valences in Ca_6FeN_5 and Ca_6MnN_5, both containing D_{3h} $[MN_3]^{6-}$ units, are also anomalously high. From the anion geometry in Sr_3CrN_3 and Ba_3CrN_3 we would expect these materials to be paramagnetic. The compound Ca_3CrN_3, purported to contain low-spin Cr^{3+}, exhibits an intriguing magnetic behaviour with temperature suggesting antiferromagnetic interactions;[3] Ca_3VN_3, however, is diamagnetic as might be expected.[4] We are currently engaged in an extensive survey of the magnetic properties of 313 and 615 materials and hope to relate these properties more fully to the crystal chemistry of these nitrides.

Acknowledgements

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