Synthesis and Structure of Ca_6MnN_5: A New Nitridomanganate with Planar $[MnN_3]^{6-}$ Anions

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The new ternary nitride Ca_6MnN_5 has been synthesized by the solid state reaction of Ca_3N_2 with Mn_4N and characterized by powder X-ray diffraction. Ca_6MnN_5 crystallizes in the hexagonal space group *P63/mcm* (a = 6.2269(1) Å, c = 12.3122(1) Å, Z = 2) and is isostructural with Ca_6FeN_5 and Ca_6GaN_5. Manganese(III) forms trigonal planar $[MnN_3]^{6-}$ units analogous to carbonate anions, which lie in planes parallel to the c axis, sandwiched between layers of Ca−N polyhedra. Calcium is coordinated to five nitrogens in a distorted square pyramidal geometry. Interestingly, at room temperature the material is diamagnetic.

Introduction

Recently there has been a great deal of interest in the chemistry of ternary transition metal nitrides. Several researchers 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 which are often unique to ternary nitride structures. Of particular interest 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] (M = Fe, Ga). These materials contain M^{3+} coordinated to three nitrogens and have structures consisting of sheets of $[MN_3]^{6-}$ planar triangular units separated by alkaline earth cations.

The 313 materials exist in two forms depending on the alkaline earth cation.[8] Strontium and barium form hexagonal structures in which the $[MN_3]^{6-}$ units (M = Cr, Mn, Fe)[4,6,8] are triangles of D_{3h} symmetry whereas calcium forms an orthorhombic structure in which the trigonal planar $[MN_3]^{6-}$ units (M = V, Cr, Mn) are of C_{2v} symmetry.[3,5,7] The calcium phases Ca_3VN_3 and Ca_3CrN_3 appear to contain low-spin transition metal ions.[3,5] Of the 313 materials, only these two calcium materials have been studied by magnetic measurements. Ca_3VN_3 is paramagnetic, but Ca_3CrN_3 appears to show antiferromagnetic behavior below 400 K.[3,5]

The 615 materials have been less extensively studied. The two reported nitrides, Ca_6GaN_5 and Ca_6FeN_5, were prepared as single crystals and studied by X-ray diffraction. These ternary nitrides form hexagonal structures containing $[MN_3]^{6-}$ units with D_{3h} symmetry. In these materials, the sheets of $[MN_3]^{6-}$ groups are sandwiched between layers of (NCa_3^{3+}) octahedra. As part of ongoing research into the structure and physical properties of ternary nitride materials, we report here the synthesis and structural characterization of Ca_6MnN_5, a new 615 phase containing trigonal planar $[MN_3]^{6-}$ units.

Experimental Section

Starting Material. The starting material Ca_3N_2 was prepared by the reaction of the molten alkaline earth metal−sodium alloy with dried nitrogen at 600 °C. The alloy was made by adding clean Ca 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 600 °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 calcium nitride containing negligible amounts of the alkaline earth oxide. The reaction yielded crystalline samples of dark red Ca_3N_2. The identity of Ca_3N_2[10] was confirmed by powder X-ray diffraction (PXD).

Synthesis of Ca_6MnN_5. A polycrystalline sample of Ca_6MnN_5 was prepared by the high-temperature solid state reaction of the binary alkaline earth nitride and manganese nitride (Mn_4N) (99.5%) powders. All preparations were carried out in a purified argon-filled glovebox. The Ca_3N_2 and Mn_4N powders were thoroughly mixed, ground together in an 8:1 molar ratio, and pelleted using a hand press. The pellet was placed in a small alumina crucible within a larger stainless steel crucible which was subsequently welded closed under purified argon. Preliminary experiments in which the pellet was placed directly in the stainless steel crucible, or in which the pellet was wrapped in a molybdenum tube within the crucible, produced a secondary phase which could not be identified by PXD. 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 nitrides with the alumina crucible, and the resulting powder of Ca_6MnN_5 was brick red/burgundy in color.

Characterization and Structure Determination. PXD data were collected using a Philips XPERT Θ−2Θ diffractometer with Cu K_α radiation. In each case, the sample was loaded in a nitrogen-filled

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Table 1. Final Crystallographic Results for Ca_6MnN_5

Space Group $P63/mcm$; $a = 6.2269(1)$ Å, $c = 12.3122(1)$ Å

atom	site	x	y	z	B^a/Å^2
Ca	12k	0.6052(1)	0	0.1182(1)	0.79(3)
Mn	2a	0	0	0.25	0.53(5)
N1	4d	0.6667	0.3333	0	1.61(19)
N2	6g	0.2822(7)	0	0.25	0.31(12)

$R_I = 3.82\%$, $R_p = 8.42\%$, $R_{wp} = 11.46\%$, $R_e = 1.37\%$

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

glovebox onto an aluminum slide contained in an aluminum 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. The sample of Ca_6MnN_5 was shown to contain a small amount of CaO and Mn metal. These impurities are to be expected from the starting ratios which generate Ca, Mn, and N_2 as additional products. The remaining peaks of each pattern were indexed by comparison with a theoretical powder pattern based on Ca_6FeN_5 generated by LAZY PULVERIX[11] and by using a combination of the PC software programs VISSER,[12] DICVOL91,[13,14] and TREOR90.[15] Lattice parameters were refined by least-squares fitting of PXD data.

Diffraction data suitable for Rietveld refinement were collected over the range 5−100° 2Θ with step size 0.02° 2Θ. Scans were run for approximately 14 h. A full-profile Rietveld refinement[16] of Ca_6MnN_5 was performed using the Philips PC RIETVELD PLUS[17,18] package with the Ca_6MN_5 (M = Ga, Fe) structures as initial models and with cell parameters obtained from least-squares fitting of PXD data. Initial cycles in the refinement of Ca_6MnN_5 allowed for the variation of the scale factor, zero point, lattice parameters, and background coefficients. 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. Impurity phases of CaO and Mn were simultaneously refined, and quantitative analysis of the diffraction data running as part of the PC RIETVELD PLUS package yielded weight percentage values of 0.3% CaO and 0.5% Mn.

Magnetic Measurements. Magnetic susceptibility measurements were performed at room temperature using a Johnson Matthey magnetic susceptibility balance. Samples (ca. 0.15 g) of Ca_6MnN_5 were thoroughly ground and loaded into preweighted 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, a value for the total molar susceptibility, χ_M, of -9.10×10^{-3} emu was obtained for the nitride, suggesting, perhaps surprisingly, that the material is intrinsically diamagnetic.

Results and Discussion

The final crystallographic results for Ca_6MnN_5 are shown in Table 1. An observed, calculated, and difference plot for the refinement of Ca_6MnN_5 is shown in Figure 1.

Ca_6MnN_5 (Figures 2 and 3) is isotypic with Ca_6GaN_5 and Ca_6FeN_5[9] and consists of Ca^{2+} cations and $[MnN_3]^{6-}$ nitridomanganate anions. Planes of isolated trigonal planar $[MnN_3]^{6-}$ groups are arranged perpendicular to the [001] plane. The trigonal planar groups are oriented in the same direction within layers but are arranged in an orientation diametrically opposite to that of the triangles in neighboring sheets, displaced by 0.5 along z. Each sheet of $[MnN_3]^{6-}$ triangles is sandwiched between a layer of edge-connected $(NCa_3{}^{3+})$ octahedra. Such an arrangement creates a layer stacking sequence of [..ABAC..] along c as observed for Ca_6FeN_5 and Ca_6GaN_5 and as can be clearly seen in Figure 2. These triangular units are of D_{3h} point symmetry as in the other 615 structures and as in the A_3FeN_3, A_3MnN_3, and A_3CrN_3 materials (A = Sr, Ba).[4,6,8] Interestingly, the triangular $[MN_3]^{6-}$ units in the orthorhombic Ca 313 materials, Ca_3VN_3, Ca_3CrN_3, and, perhaps significantly Ca_3MnN_3, are distorted with C_{2v} point symmetry.[3,5,7] Clearly, the space group symmetry does not allow such a distortion of the Mn−N triangle in Ca_6MnN_5. Interestingly the room-temperature magnetic susceptibility measurements suggest there are no unpaired d electrons ($S = 0$). Assuming Mn^{3+}, an $S = 0$ state could only exist for C_{2v} symmetry and may imply a small monoclinic distortion undetected in this study or previous X-ray work. Further studies are currently underway to investigate this possibility.

Important interatomic distances in Ca_6MnN_5 are shown in Table 2. Relevant bond angles around the metal atoms and nitrogen atoms are described in Tables 3 and 4.

The Mn−N bond length in the $[MnN_3]^{6-}$ units compares well with the analogous distance in Ca_6FeN_5 (Fe−N = 1.770(15) Å)[9] but is smaller than the mean Mn−N bond length in the 313 material Ca_3MnN_3 (1.796(5) Å).[7] It is interesting to note, however, that in hexagonal Sr_3MnN_3 and Ba_3MnN_3 the Mn−N bond lengths in the D_{3h} triangles are smaller and closer to the distance found in Ca_6MnN_5 (bond lengths of 1.741(13) and 1.737(12) Å for A = Sr and Ba, respectively).[6] To date, there are no previously reported examples of transition metals that form both 313 and 615 phases, and hence a comparison of the changes in M−N distances in other materials cannot be made at this stage.

Calcium is coordinated to five nitrogen atoms in a distorted square-based pyramidal geometry with distances ranging from ~2.4 to ~2.7 Å. The square-based pyramid has two long bonds (Ca−N2) and two short bonds (Ca−N1) in the basal plane which is buckled rather than flat (N1−Ca−N2 = 159.23(9)°). The relatively short Ca−Mn distances in Ca_6MnN_5, however, suggest metal−metal interactions, and similarly short distances are observed in the other 615 phases.[9] The mean Ca−N bond distance is 2.569(2) Å, which is larger than that observed in the binary nitrides α−Ca_3N_2[10] (2.46 Å), Ca_2N (2.433 Å),[19] and $Ca_{11}N_8$ (2.434 Å).[20] The average Ca−N bond length is close to those in other calcium ternary nitride phases, however, where the reported distances are consistently longer. For example, the mean Ca−N distances in the Ca_3MN_3 phases are 2.564, 2.490(3), and 2.529(2) Å for M = V, Cr, and Mn, respectively,[3,5,7] whereas in Ca_6GaN_5 and Ca_6FeN_5 the distances are 2.56(1) and 2.56(2) Å.[9]

Bond valence calculations were performed for the calcium and manganese sites using bond length parameters derived for nitrides by Brese and O'Keeffe.[21,22] The bond valence parameters, R_{ij}, for Ca−N and Mn−N were taken as 2.14 and 1.87 Å, respectively, and the valences of the two cations in Ca$_6$-

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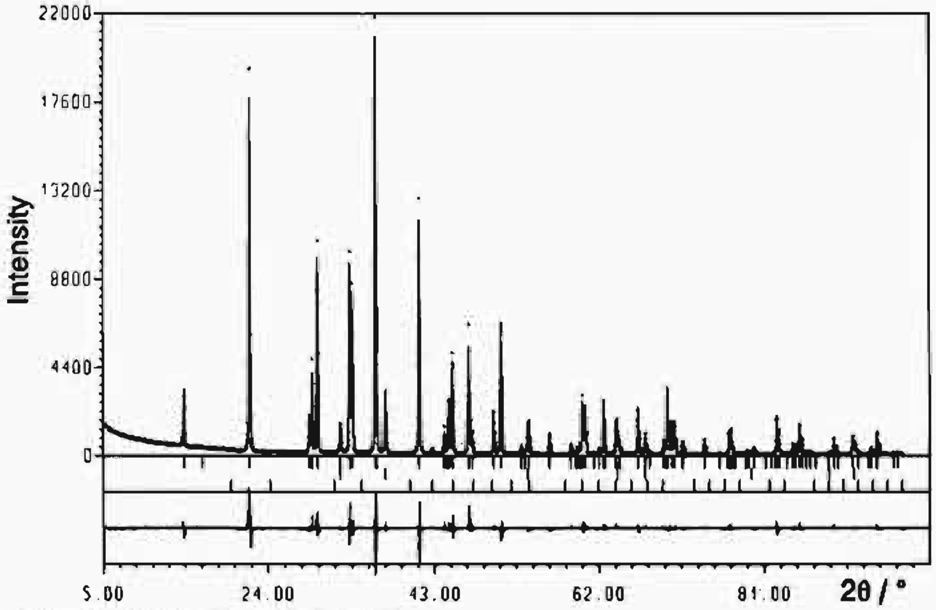

Figure 1. Observed, calculated, and Difference plot of Ca_6MnN_5.

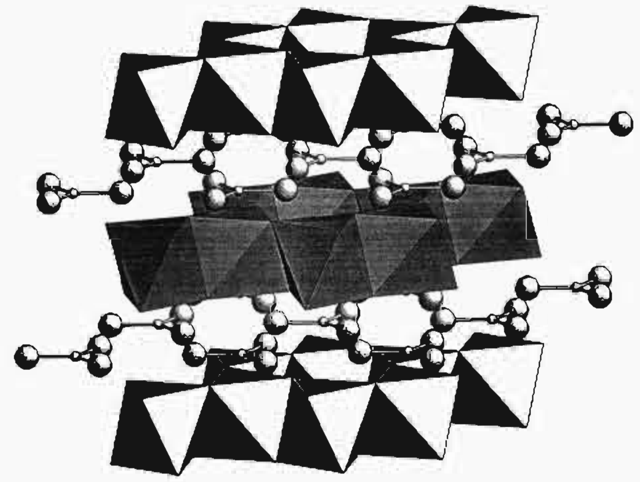

Figure 2. Ca_6MnN_5 viewed down the 100 direction showing layers of discrete $[MnN_3]^{6-}$ triangles sandwiched between layers of (NCa_3^{3+}) octahedra.

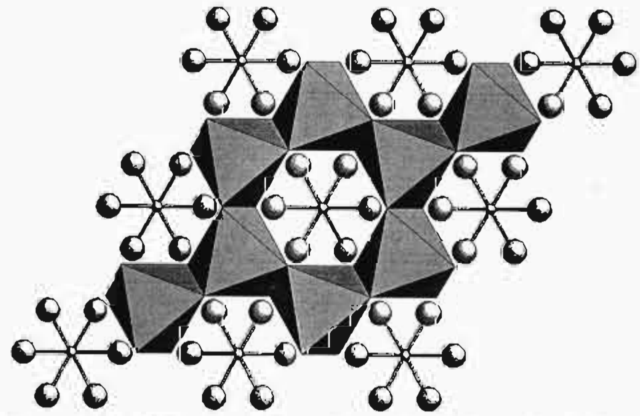

Figure 3. Ca_6MnN_5 viewed down the *c* axis showing edge-sharing (NCa_3^{3+}) octahedra and successive layers of oppositely aligned $[MnN_3]^{6-}$ triangles.

Table 2. Interatomic Distances in Ca_6MnN_5

atoms	number	dist/Å
Ca−N1	2	2.4039(6)
Ca−N2	1	2.583(3)
Ca−N2	2	2.728(2)
Mn−N2	3	1.757(4)
Ca−Mn	6	2.9455(7)

Table 3. Bond Angles around Ca and Mn in Ca_6MnN_5

atoms	angle/deg	atoms	angle/deg
N1−Ca−N1	96.79(1)	N2−Ca−N2	94.42(8) × 2
N1−Ca−N2	99.68(1) × 2	N2−Ca−N2	67.83(11)
N1−Ca−N2	95.77(2) × 2	N2−Mn−N2	120 × 3
N1−Ca−N2	159.23(9) × 2		

Table 4. Bond Angles around N1 and N2 in Ca_6MnN_5

atoms	angle/deg	atoms	angle/deg
Ca−N1−Ca	87.13(3) × 6	Ca−N1−Ca	164.14(2) × 3
Ca−N1−Ca	104.84(3) × 3	Ca−N1−Ca	83.20(3) × 3
Ca−N2−Mn	78.82(2) × 4	Ca−N2−Ca	77.80(3)
Ca−N2−Mn	141.09(2) × 2	Ca−N2−Ca	102.57(2) × 2
Ca−N2−Ca	77.13(2) × 4	Ca−N2−Ca	157.65(3) × 2
Ca−N2−Ca	121.61(1) × 4	Ca−N2−Ca	72.97(2) × 2

MnN_5 were evaluated. Calculations yielded oxidation states of 1.7 for Ca and 4.1 for Mn. These valences are lower and higher, respectively, than expected. The calculations suggest that the Ca−N and Mn−N sublattices are overstretched and compressed, respectively. It is worth noting that much the same valences are obtained from the bond lengths in Ca_6FeN_5 (1.7 for Ca and 4.1 for Fe) whereas in Ca_6GaN_5 the Ca and Ga atoms are both underbonded (valences of 1.8 for Ca and 2.2 for Ga).[9] The valence sums for the nitrogens in Ca_6MnN_5, N1 and N2, were also calculated and gave values of −2.9 and −2.8, respectively.

It is of interest to compare the cation site valences in Ca_6MnN_5 with those calculated from bond lengths in 313 phases. In Ca_3MnN_3,[7] calciums on the Ca1 and Ca2 sites have oxidation states of 1.8 and 1.7, respectively, whereas Mn coordinated to N in distorted C_{2v} triangles has a calculated oxidation state of 3.7. These are similar to the valences obtained for the alkaline earth sites and transition metal sites in the other Ca_3MN_3 phases (M = V, Cr).[3,5] In the hexagonal A_3MnN_3 phases (A = Sr, Ba),[6] a similar pattern of underbonded A sites and overbonded Mn sites is observed. The alkaline earth sites have calculated valences of 1.3 (a low value similar to that calculated for Sr_2N)[23]

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and 1.6, respectively. The manganese sites in these materials have calculated valences of 4.2 and 4.3 for Sr and Ba, respectively.

In summary, we have synthesized a new ternary nitride containing planar $[MnN_3]^{6-}$ anions by the high-temperature reaction of the respective binary nitrides. Ca_6MnN_5 is isostructural with the previously reported ternary materials Ca_6FeN_5 and Ca_6GaN_5.[9] We will shortly be performing more extensive magnetic measurements on 615 materials with the intention of relating the magnetic behavior of these nitrides to their crystal structures and evaluating the symmetry of the $[MN_3]^{6-}$ anions.

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Supporting Information Available: A list of X-ray diffraction data for Ca_6MnN_5, including *d* spacings, observed and calculated intensities, and indexed reflections, and a compilation of the final cycles in the refinements of Ca_6MnN_5 showing final crystallographic parameters and esd's (8 pages). Ordering information is given on any current masthead page.

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