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Synthesis, Structure, and Properties of Ca_2ZnN_2

MING Y. CHERN AND F. J. DiSALVO*

Department of Chemistry, Cornell University, Ithaca, New York 14853

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We report the synthesis and physical properties of the new ternary nitride Ca_2ZnN_2, prepared by the reaction of Ca_3N_2 and Zn in N_2 gas at 680°C. The structure, determined by X-ray powder diffraction and refined by Rietveld profile analysis, is tetragonal (*I4/mmm*) with $a = 3.5835(4)$ Å, $c = 12.6583(7)$ Å, and $Z = 2$. The structure features condensed nitrogen-centered metal octahedra and a linear coordination of Zn by two nitrogen atoms. Conductivity and magnetic measurements show that Ca_2ZnN_2 is insulating and diamagnetic. © 1990 Academic Press, Inc.

Introduction

Both calcium and zinc form nitrides, Ca_3N_2 and Zn_3N_2, respectively. They adopt the same structure which is a supercell of anti-fluorite, i.e., anti-CaF_2 (*1*, *2*). In the nitride structure six metal atoms and two vacancies occupy the fluorine sites, and four nitrogen atoms occupy the calcium sites. The metal atoms and vacancies are distributed in an ordered manner so that the fluorine sites along one body diagonal are not occupied. The unit cell consists of three types of $M_6V_2N_4$ units (M; metal; V; vacancy) with the vacancies ordered along different body diagonals, leading to a cubic unit cell with a volume eight times larger than that of the anti-CaF_2 basis (*3*).

The nitrogen in Ca_3N_2 and Zn_3N_2 is surrounded by six metal atoms in a distorted octahedron, and the metal is tetrahedrally coordinated to four nitrogen atoms. We have synthesized a new ternary nitride Ca_2ZnN_2 which does not adopt an anti-CaF_2 structure, but in which the nitrogen is still coordinated to six metal atoms (one zinc and five calcium atoms), and the calcium and the zinc are only coordinated to five and two nitrogen atoms, respectively. This paper reports the synthesis, structure, and magnetic properties of Ca_2ZnN_2.

Experimental

Synthesis

All manipulations were carried out in an argon-filled glove box. Calcium nitride was first prepared by heating calcium in N_2 gas at 1000°C. Then a pressed pellet of finely ground Ca_3N_2 and Zn powder was heated at 680°C in N_2 to make the compound. Since zinc has an appreciable vapor pressure at that temperature (10^{-1} Torr), 10% excess zinc was added to compensate for its loss. Any excess unreacted zinc simply vaporizes and leaves the pellet since Zn_3N_2 cannot be formed by heating Zn metal in N_2 gas (*2*). The weight difference of the pellet before and after the reaction is consistent with the weight loss of the 10% excess zinc and the weight gain of nitrogen based on the stoichiometry Ca_2ZnN_2. (The more accurate determination of the chemical formula is described in the next section.) Ca_2ZnN_2 is an

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air-sensitive, brown powder. An ohmmeter registered 850 kohm when the resistance of a pressed pellet of the sample was measured, indicating that Ca_2ZnN_2 is insulating.

Unit Cell and Stoichiometry Determination

X-ray powder diffraction data were collected with a Scintag XDS 2000 diffractometer using copper $K\alpha$ radiation over a 2θ range 5 to 100° at a scanning interval of 0.01° and a count time of 6 sec per interval. Both $K\alpha_1$ and $K\alpha_2$ lines were used for the structure refinement. The sample was loaded in an aluminum holder and covered with a 0.5-mil-thick layer of Mylar in a dry box to avoid air exposure. The Mylar sheet was supported by two semicircular disks standing perpendicular to the sample so that the absorption due to the Mylar is uniform and small over the whole 2θ range.

The pattern was indexed on a tetragonal unit cell by using the program TREOR (*6*) (a = 3.5835(4) Å, c = 12.6583(7) Å), and the only systematic absences, $h + k + l = 2n$, indicate that the unit cell is body-centered. No impurity phases could be detected by X-ray diffraction.

When a unit cell is not too large and contains only a small number of atoms, the stoichiometry can often be determined from the density of the compound and the unit cell volume, assuming a small number of formula units per unit cell, Z. We obtained the density of the powdered product using a previously described density apparatus in the glove box (*4*), and the measured density is 3.49 g/cm^3. Since the cell is body-centered, there must be an even number of formula units in the cell. Additionally, since the sample is single phase and the mass of the products indicates a cation ratio of Ca_2Zn, there must be at least four Ca and two Zn atoms in the unit cell and several nitrogen atoms. If the Ca and Zn both are in oxidation state 2^+, then four nitrogen atoms would also be in the unit cell. Using the unit cell volume of 162.43 Å,[3] we obtained a theoretical density of 3.55 g/cm^3—only 1.7% higher than the measured value.

Since nitrogen is a light element, the nitrogen stoichiometry cannot be accurately determined by the density alone. We used the modified Dumas method to measure the nitrogen content (*5*). The sample was heated at 1100°C in a CO_2 flow and was converted into ZnO, CaO, and N_2. The measured volume of N_2 then indicates a stoichiometry of $Ca_2ZnN_{1.96}$.

Structure Determination

There are eight tetragonal space groups which are body-centered and do not have additional systematic absences. Since there are only two zinc atoms in the unit cell, we chose zinc to occupy the following fixed positions: 0,0,0 and 1/2,1/2,1/2. For all these eight space groups, complete occupation of the most general positions would result in eight or more calcium or nitrogen atoms in the unit cell; therefore, calcium and nitrogen must occupy special positions. By trial and error we determined that of all these special positions in these eight space groups a reasonable fit to the intensities could be obtained only if the calcium and nitrogen positions are of the type $0,0,z$. Thus we initially made two inequivalent pairs of calcium and nitrogen by locating Ca at $0,0,z_1$; $1/2,1/2,1/2 + z_1$ and $0,0,z_2$; $1/2,1/2,1/2 + z_2$ with $z_1 \sim 1/3$ and $z_2 \sim 2/3$, and N at $0,0,z_3$; $1/2,1/2,1/2 + z_3$ and $0,0,z_4$; $1/2,1/2,1/2 + z_4$ with $z_3 \sim 1/6$ and $z_4 \sim 5/6$. Then we used a Rietveld profile analysis to refine the z positional parameters along the c-axis with the use of the generalized crystal structure analysis system (GSAS) (*7*). The variables refined include a scale factor, 12 Fourier background coefficients, a diffractometer zero correction, lattice constants, atomic coordinates, occupation numbers, six peak profile parameters (GU, GV, GW, LX, LY, LZ), and isotropic thermal factors. The best result was obtained when the two

TABLE I

RESULTS OF THE REFINEMENT OF Ca_2ZnN_2

Space group

I4/mmm

Lattice constants

$a = 3.5835(4)$ Å, $c = 12.6583(7)$ Å

Atomic Coordinates

Atom	Symmetry position	x	y	z
Zn	(2*a*)	0	0	0
Ca	(4*e*)	0	0	0.3360
N	(4*e*)	0	0	0.1455

z-coordinates of the calcium pairs and the two z-coordinates of the nitrogen pairs are related by inversion, i.e., $z_1 = -z_2$, $z_3 = -z_4$, and the final refinement converges with $R_p = 12.4$ and $R_{wp} = 16.5$. This indicates that the Ca and N are in positions of multiplicity 4, and are of Wycoff type *e*. Space group *I4/mmm*, No. 139, is therefore assigned since it is the group with the highest number of symmetry operations among the body-centered space groups having the above special positions (4*e*). The refined results are shown in Table I. The observed intensities along with the calculated profile are plotted in Fig. 1. Table II contains the observed and calculated integrated intensities. The occupation numbers were fixed to be integers in the last refinement because they do not significantly deviate from the ideal values, i.e., 2, 1, and 2 for Ca, Zn, and N, respectively. The thermal factors were

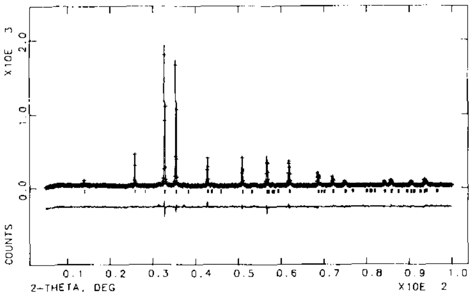

FIG. 1. The result of the Rietveld refinement for Ca_2ZnN_2 (X-ray intensity versus 2-θ). The experimental data are represented by crosses and the calculated profile by the solid lines. The difference curve is shown at the bottom.

TABLE II

X-RAY POWDER DIFFRACTION DATA ($\lambda_{CuK\alpha_1}$ = 1.540560 Å) FOR Ca_2ZnN_2

hkl	d_{obsd} (Å)	d_{calcd} (Å)	I_{obsd}	I_{calcd}
002	6.3168	6.3292	3	3
101	3.4441	3.4480	18	18
004	—	3.1646	<1	<1
103	2.7292	2.7314	100	100
110	2.5320	2.5339	79	81
112	2.3508	2.3524	3	2
006	2.1088	2.1097	23	21
105	2.0665	2.0677	3	2
114	—	1.9780	<1	<1
200	1.7913	1.7918	27	26
202	—	1.7240	<1	1
116	1.6205	1.6213	37	34
107		1.6144		2
211	1.5891	1.5899	4	3
008	—	1.5823	<1	1
204	—	1.5592	<1	<1
213	1.4978	1.4982	33	32
206	1.3651	1.3657	20	19
215	—	1.3541	<1	1
118	—	1.3421	<1	1
109	1.3087	1.3092	14	13
220	1.2666	1.2670	8	8
0010	—	1.2658	<1	<1
222	—	1.2423	<1	<1
217	—	1.1994	<1	<1
301	—	1.1892	<1	<1
208	—	1.1860	<1	1
224	—	1.1762	<1	<1
303	1.1490	1.1493	8	7
310	1.1328	1.1332	11	11
1110	—	1.1324	<1	<1
312	—	1.1155	<1	<1
1011	—	1.0956	<1	<1
226	1.0859	1.0862	9	9
305	—	1.0803	<	<1
314	—	1.0669	<1	<1
219	1.0566	1.0571	15	12
0012		1.0549		2
2010	—	1.0339	<1	<1

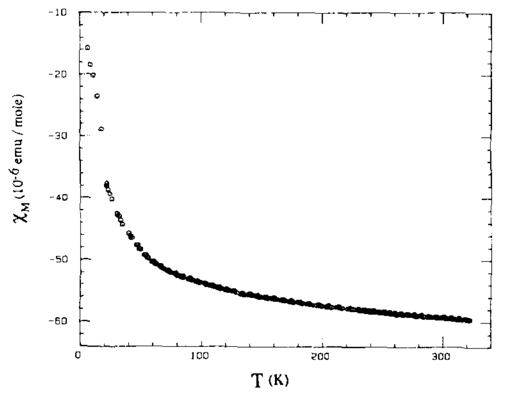

FIG. 2. The temperature dependence of the magnetic susceptibility of Ca_2ZnN_2 shows that a very low level of paramagnetic impurities are present in the sample.

also fixed to be 0.005 Å^2 for all the atoms because small negative thermal factors otherwise occurred while only slightly reducing R_p to 12.3. Since the negative thermal factors are small and R_p is improved by only a very small amount, we do not take these negative numbers to indicate a problem with the structure, but rather a result of the statistics of small peaks and a nonideal peak profile.

Magnetic Susceptibility Measurement

The magnetic susceptibility of Ca_2ZnN_2 was measured between 320 and 4 K by the use of a Faraday balance. The susceptibility at room temperature was measured at different fields, and a field-dependent susceptibility was found, indicating some contamination by ferromagnetic impurities. We subtracted the impurity signal from the data by the method of Owen and Honda (*8*), and the corrected data are shown in Fig. 2. (The contamination was equivalent to only 10^{-6} g of iron.) A small amount of paramagnetic impurities showing Curie-like behavior is also obvious from the increasing susceptibility at low temperatures. The intrinsic susceptibility of the sample, -63.74×10^{-6} emu/mole, was obtained by extrapolating the data to high temperature.

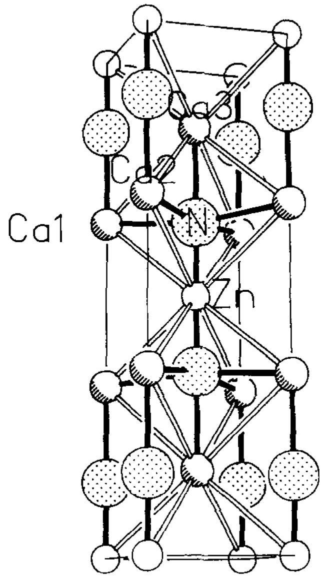

FIG. 3. The crystal structure of Ca_2ZnN_2. The N is octahedrally coordinated to one Zn and five Ca atoms; the Ca has five nearest neighbors; the Zn is linearly coordinated to two nitrogen atoms.

Results and Discussion

The crystal structure of CA_2ZnN_2 is shown in Fig. 3, and the bond distances are listed in Table III. In this compound the nitrogen is octahedrally coordinated by one zinc atom and five calcium atoms. Figure 4 shows how these nitrogen-centered octahedra stack together. The structure can be visualized in the following way. First, edge-sharing octahedra form a two-dimensional

TABLE III

INTERATOMIC DISTANCES FOR Ca_2ZnN_2

Ca1–Ca2	3.5835 Å	Ca2–Ca3	3.3414 Å
N–Ca1	2.5449 Å	N–Ca3	2.4128 Å
N–Zn	1.8418 Å	Ca–Zn	3.2759 Å

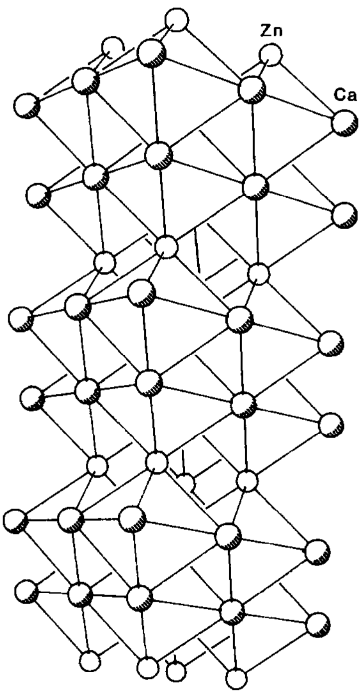

FIG. 4. An extended view of Ca_2ZnN_2. The structure consists of edge-sharing octahedra linked by the zinc at the corners. The nitrogen in the center of the octahedron is not shown.

sheet. A second identical sheet is then added to the first by translating it by one Ca–N distance and joining it to the first with all edge-sharing contacts. The metal atoms at the top and bottom of these double sheets are zinc and the remainder are calcium. These double sheets are then joined by corner-sharing zinc atoms to make the three-dimensional structure.

Octahedral coordination of nitrogen by six metal atoms is frequently observed in the known ternary nitrides containing calcium. Examples are CaNiN (*9*), where the N is coordinated to two Ni and four Ca atoms; Ca_3BiN, where the N is surrounded by six Ca atoms (*10*); the solid solution $Ca_xTi_{1-x}N$, where (Ca_xTi_{1-x}) and N form a sodium chloride structure (*11*); Ca_3CrN_3, where the N is bonded to one Cr and five Ca atoms (*12*); CaGaN, where the N has six nearest neighbors, one Ga and five Ca, (*13*); and Ca_4In_2N, where the N is in the octahedral sites built by six calcium atoms (*14*). This systematic trend is useful for building structural models to solve the structure of other ternary calcium nitrides. The only exception to the rule is a Zintl phase $CaGeN_2$, where $(GeN_2)^{2-}$ adopts a β-cristobalite, SiO_2, structure, with the calcium ions "stuffed" in the remaining tetrahedral sites; therefore, the N is linearly coordinated to two Ge with a very short Ge–N distance of 1.85 Å (*15–17*). This exception is due to the strong covalency between Ge and N.

Another interesting aspect of this compound is that the zinc is linearly coordinated to two nitrogen atoms. This linear coordination of Zn is quite unusual in solid state compounds. The average Ca–N distance, 2.48 Å, is close to that in Ca_3N_2, 2.47 Å (*1*). However, the Zn–N distance, 1.84 Å, is far shorter than that in Zn_3N_2 (*2*), 2.10 Å. This must be due to the decrease in the coordination number of the zinc from six to two. The Ca–Zn distance, 3.28 Å, is very close to those in Ca_3Zn and CaZn, 3.27 and 3.26 Å, respectively (*18*).

Ca_2ZnN_2 is isostructural with Na_2HgO_2 (*19*) and Na_2PdH_2 (*20*), where Hg and Pd are also linearly coordinated to two oxygen and two hydrogen atoms, respectively. One might think that the cadmium analogue of Ca_2ZnN_2 could be made, but the attempt has not yet been successful.

Since Ca_2ZnN_2 is an insulator, one would expect that the magnetic susceptibility is close to the sum of those of the ions: Ca^{2+}, Zn^{2+}, and N^{3-}. The value thus obtained (*21*), -71.32×10^{-6} emu/mole, is dominated by N^{3-} and is close to the measured one, -63.74×10^{-6} emu/mole. The small difference may be due to the partial covalent character of the bonding. As the bonding becomes more covalent, the effective radius of "N^{3-}" as well as its diamagnetic susceptibility decrease.

In summary we have synthesized a new ternary nitride phase Ca_2ZnN_2. It is insulating and diamagnetic; the structure is based on condensed nitrogen-centered metal octahedra and has an unusual low coordination number for zinc of two.

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