

# The Crystal Structures of $\text{Mg}_3\text{N}_2$ and $\text{Zn}_3\text{N}_2$

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**The structures of  $\text{Mg}_3\text{N}_2$  and  $\text{Zn}_3\text{N}_2$  have been refined from neutron time-of-flight powder diffraction data. These compounds have the antibixbyte structure and are the first such to be fully refined. The space group is  $Ia\bar{3}$ ,  $a = 9.9528(1)$  Å ( $\text{Mg}_3\text{N}_2$ ) and  $9.7691(1)$  Å ( $\text{Zn}_3\text{N}_2$ ). A revised bond valence parameter for Mg–N bonds is suggested.** © 1997 Academic Press

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## INTRODUCTION

There has recently been a resurgence of interest in solid state nitrides and many new compounds have been characterized (1–4) but there are still some surprising gaps in our knowledge of the structures of binary metal nitrides. Nitrides  $M_3\text{N}_2$  with  $M = \text{Be}, \text{Mg}, \text{Ca}$  were reported (5) in 1933 to have the *anti*-bixbyte structure although only the lattice parameters were determined.  $\text{Zn}_3\text{N}_2$  and  $\text{Cd}_3\text{N}_2$  were reported (6) to also have this structure in 1940, but again the structures were not refined. Some of the corresponding phosphides and arsenides were found at the same time (5, 7) to also have the antibixbyte structure. *Approximate* structures were later reported for  $\text{Ca}_3\text{N}_2$  (8) and  $\text{Mg}_3\text{N}_2$  (9), but in these studies no allowance was made for atomic displacements (i.e., no “temperature” factors) and all  $M$ –N distances were constrained to be equal.

The cubic bixbyte, or “C-type rare earth oxide,” structure has been carefully refined for many oxides such as  $\text{Sc}_2\text{O}_3$  [at least six times, most recently by (10)], which is sometimes considered the “type” structure,  $\text{Y}_2\text{O}_3$  [at least seven times, most recently by (11)],  $\text{In}_2\text{O}_3$ ,  $\text{Tl}_2\text{O}_3$ , and heavier rare earth sesquioxides. The details of the structure have been the topic of some discussion (12, 13) so it is somewhat surprising to find that there have been no investigations of the corresponding antistructure (i.e., that in which the roles of cation and anion are interchanged) except for the two very approximate studies mentioned above. We note that the situation is rather similar to that for the  $\text{Na}_3\text{As}$  structure type for which many representatives were reported over 50 years ago, but for which there were no modern quantitative studies. In that case a recent reexamination (14) showed that the originally assigned unit cell and space group were in fact incorrect. In

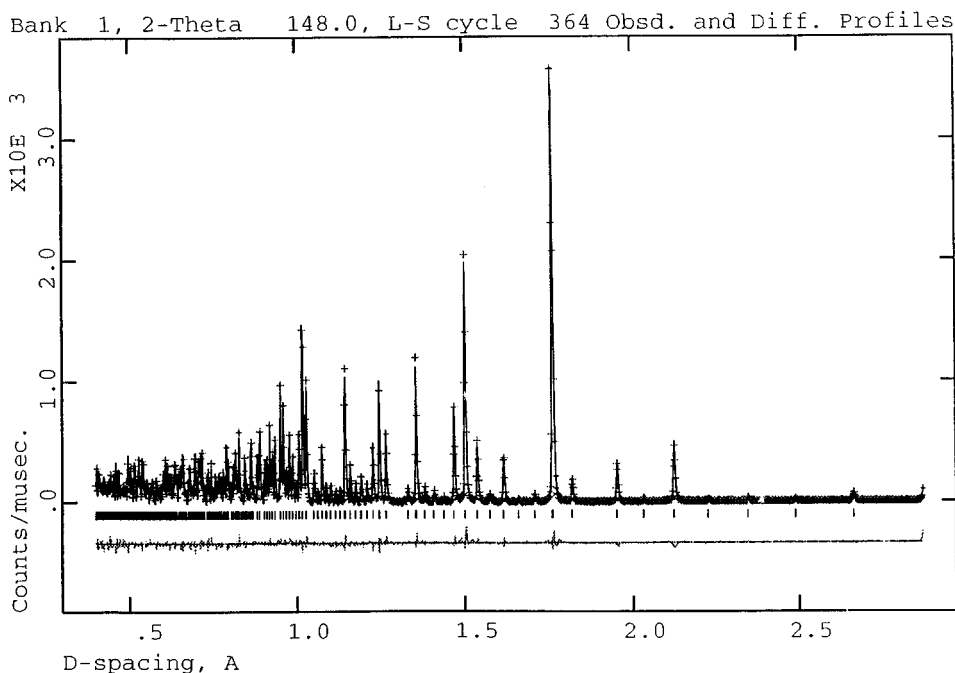
view of the fact that it has recently been shown (15) that properties such as the equation of state of simple sulfides such as  $\text{MgS}$  and  $\text{CaS}$  can be successfully modeled using an ionic model, accurate structural data for simple nitrides should be of interest in that connection also.

In this paper we report the full refinement, with anisotropic atomic displacement parameters, of the structures of  $\text{Mg}_3\text{N}_2$  and  $\text{Zn}_3\text{N}_2$  by time-of-flight powder neutron diffraction. The antibixbyte structure, in which the metal atoms are in tetrahedral sites of an approximately cubic close packed array of N atoms, is confirmed. In this cubic structure, the metal atoms are in general positions,  $48e$  of  $Ia\bar{3}$  ( $x, y, z$ ; etc.) and there are two kinds of N atom. N(1) is in position  $8b$  ( $1/4, 1/4, 1/4$ ; etc.) and N(2) is in positions  $24d$  ( $x, 0, 1/4$ ; etc.)

## EXPERIMENTAL

$\text{Mg}_3\text{N}_2$  (“99.6%”) and  $\text{Zn}_3\text{N}_2$  (“99.9%”) were obtained from Cerac Inc. In both cases X-ray powder diffraction showed that the materials were well crystalline. In the case of  $\text{Mg}_3\text{N}_2$  all lines could be indexed using an  $Ia\bar{3}$  cell; the  $\text{Zn}_3\text{N}_2$  material showed in addition a small amount of  $\text{ZnO}$ , but as this is a well-known structure, and easily allowed for in neutron powder diffraction, both the materials were studied as received.

Neutron powder diffraction data were collected at 305 K on the general purpose powder diffractometer at the intense pulsed neutron source at Argonne National Laboratory. The data were collected using the  $\pm 148^\circ$ ,  $\pm 90^\circ$ , and  $\pm 60^\circ$  detector banks, which were symmetrically summed following the collection, and which covered a  $d$ -spacing range from 0.4 to 5.7 Å. In both cases data for the three banks refined comparably and the results reported below are for the three sets combined. The structure was refined using the general structure analysis system, a Rietveld profile analysis code developed by Larson and Von Dreele (16). The structural models were refined for lattice parameters, atomic positions, and anisotropic atomic displacements. Background coefficients, scale factor, anisotropic strain terms in the profile function, and sample absorption were also refined. Table 1 reports statistics for the final



**FIG. 1.** TOF neutron diffraction profile fit to 148° bank for  $\text{Mg}_3\text{N}_2$ . The data are shown as + and the tick marks are at the Bragg positions. The solid line is the calculated profile, and the difference curve is shown at the bottom on the same scale.

refinements and Figs. 1 and 2 show observed and calculated histograms for detector bank 1, which covers most of the reflections. Table 2 reports atomic positions for the two structures. The atomic displacements were all fairly isotropic and quite close to each other so equivalent isotropic displacement parameters are also reported in Table 2.

## DISCUSSION

Previous studies (8, 9) of antibixbyite nitrides followed the original work of Pauling and Shappell (17) on bixbyite  $[(\text{Mn}, \text{Fe})_2\text{O}_3]$  itself in assuming that all metal–nonmetal bonds were of equal length. In fact in the nitrides, N is in general positions and tetrahedrally bonded to four metal atoms; accordingly there are four independent metal–nitro-

gen distances. These are reported in Table 3 from which it may be seen that there is in fact a significant range of bond lengths.

The N arrays are fairly close to ideal cubic close packing. In  $\text{Mg}_3\text{N}_2$  the 12 shortest N...N distances are 3.31–3.75 Å; the corresponding distances in  $\text{Zn}_3\text{N}_2$  are 3.31–3.61 Å.

Bond valence sums at the atoms are of interest. Using the bond valence parameters (18)  $R_{\text{MgN}} = 1.85 \text{ \AA}$  and  $R_{\text{ZnN}} = 1.77 \text{ \AA}$ , the bond valence sums (18) reported in Table 4 are determined. These are significantly less than the ideal values (2 for Zn and Mg, and 3 for N). However, it has been remarked earlier (19) that metal-rich compounds such as  $\text{Mg}_3\text{N}_2$  might be expected to have reduced stability due to metal...metal interactions, and that this in turn is reflected in longer bonds and reduced bond valence sums (20). In  $\text{Mg}_3\text{N}_2$  the shortest Mg...Mg distance is 2.72 Å; this might be compared with 2.98 Å in MgO and 3.20 Å in elemental Mg. Those of us who do not subscribe to a 100% ionic description of compounds such as  $\text{Mg}_3\text{N}_2$ <sup>1</sup> would not therefore be surprised to find some manifestation of Mg...Mg nonbonded interactions such as, in this instance, a low bond valence sum at Mg (1.83). There is a surprising lack of other well-refined structures of Mg and Zn nitrides; however, the structure of  $\text{MgSiN}_2$  has been refined from neutron powder

**TABLE 1**  
**Lattice Parameters and Refinement Statistics for  $\text{Mg}_3\text{N}_2$  and  $\text{Zn}_3\text{N}_2$**

	$\text{Mg}_3\text{N}_2$	$\text{Zn}_3\text{N}_2$
Unit cell, $a$	9.9528 (1)	9.7691 (1)
Data points	11123	11123
Reflections	1396	1308
$R_p$	0.046	0.042
$wR_p$	0.071	0.060
$\chi^2$	3.74	9.07
Variables	50	42

<sup>1</sup> e.g., Ref. (3): "the contribution of ionic bonding to the stability of nitrides is likely to be small."

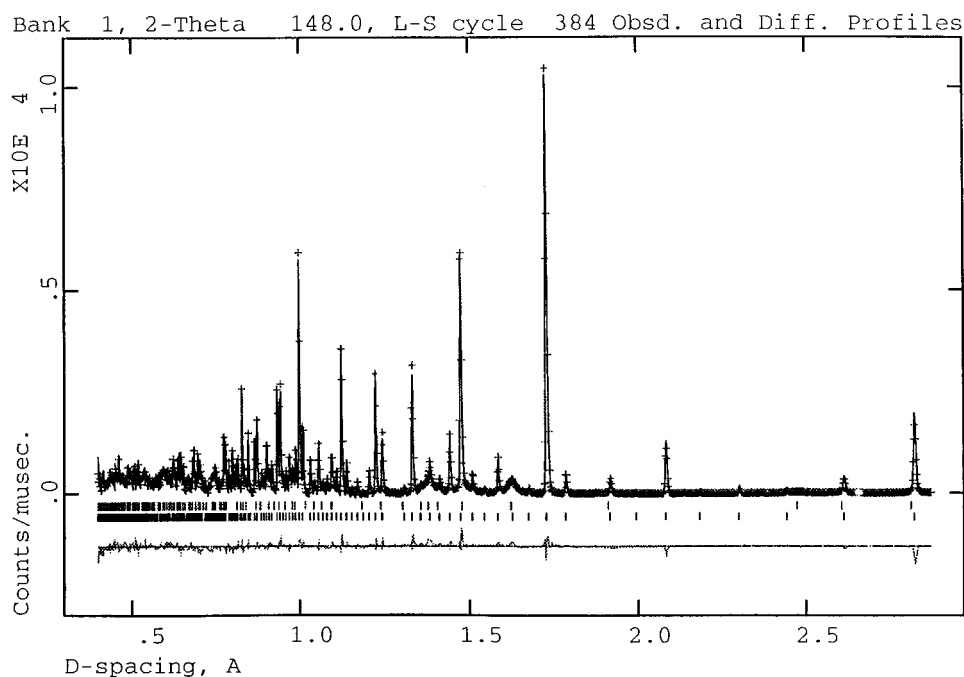


FIG. 2. TOF neutron diffraction profile fit to 148° bank for  $Zn_3N_2$ . The data are shown as  $\cdot$ . The top tick marks are at the Bragg positions for ZnO impurity and the bottom set are for  $Zn_3N_2$ . The solid line is the calculated profile, and the difference curve is shown at the bottom on the same scale.

diffraction data (21) and the structure of  $Mg_2PN_3$ , as determined from X-ray powder diffraction, has just been reported (22). In these compounds the metal/nonmetal ratio is lower than in  $Mg_3N_2$ , and Mg is again in tetrahedral coordination. The cation...cation distances are all greater than 2.95 Å. In  $MgSiN_2$  the Mg-N bond lengths are 2.059, 2.082, 2.090, and 2.115 Å (mean 2.087) and in  $Mg_2PN_3$  they are 2.017, 2.054, 2.090, and 2.179 (mean 2.085); shorter than the corresponding bond lengths in  $Mg_3N_2$  by, on average, 0.07 Å.

The Brese-O'Keeffe nitride bond valence parameters (18) were derived from a complicated interpolation scheme and

were only indirectly determined from experimental data. The value given there of  $R_{Mg-N} = 1.85$  Å should be reduced to  $R_{Mg-N} = 1.827$  Å to give bond valence sums of 2.0 at Mg in  $MgSiN_2$  and  $Mg_2PN_3$  and this value is recommended although it would, of course, make the bond valence sum at Mg even lower (1.72) in  $Mg_3N_2$ . Clearly it would be desirable to have a database of well-refined nitride structures so that bond valence parameters could be directly determined. In this context we cannot resist calling attention to the imbalance in the current situation in which oxide structures are refined, seemingly endlessly (cf. the remarks on  $Sc_2O_3$  and  $Y_2O_3$  in the Introduction), yet nitride structures scarcely at all.

TABLE 2  
Atomic Position and Isotropic Displacement ( $U_{eq}$ )<sup>a</sup> Parameters for  $Mg_3N_2$  and  $Zn_3N_2$

	x	y	z	100 $U_{eq}$
$Mg_3N_2$				
Mg	0.3890(1)	0.1520(1)	0.3823(1)	0.32(3)
N(1)	1/4	1/4	1/4	0.38(2)
N(2)	0.96951(4)	0	1/4	0.34(3)
$Zn_3N_2$				
Zn	0.3975(1)	0.1498(2)	0.3759(1)	0.43(5)
N(1)	1/4	1/4	1/4	0.27(4)
N(2)	0.9784(1)	0	1/4	0.28(4)

<sup>a</sup> $U_{eq} = (U_{11} + U_{22} + U_{33})/3$  in units of Å<sup>2</sup>.

TABLE 3  
Bond Lengths (Å) for  $Mg_3N_2$  and  $Zn_3N_2$

$Mg_3N_2$			
Mg-N(1)	2.145(1)	N(1)-Mg	2.145(1) (6 ×)
Mg-N(2)	2.084(1)	N(2)-Mg	2.084(1) (2 ×)
Mg-N(2)	2.160(1)	N(2)-Mg	2.160(1) (2 ×)
Mg-N(2)	2.179(1)	N(2)-Mg	2.179(1) (2 ×)
$Zn_3N_2$			
Zn-N(1)	2.133(2)	N(1)-Zn	2.133(2) (6 ×)
Zn-N(2)	1.996(1)	N(2)-Zn	1.996(1) (2 ×)
Zn-N(2)	2.068(1)	N(2)-Zn	2.068(1) (2 ×)
Zn-N(2)	2.262(1)	N(2)-Zn	2.262(1) (2 ×)

**TABLE 4**  
Bond Valence Sums at Atoms in Mg<sub>3</sub>N<sub>2</sub> and Zn<sub>3</sub>N<sub>2</sub>

Mg <sub>3</sub> N <sub>2</sub>	Mg	1.83	N(1)	2.70	N(2)	2.75
Zn <sub>3</sub> N <sub>2</sub>	Zn	1.63	N(1)	2.25	N(2)	2.51

Finally it is remarked that the structures of these two antibixbyite structures are close to those of typical bixbyites. Table 5 compares the free atomic position parameters for Mg<sub>3</sub>N<sub>2</sub> and Zn<sub>3</sub>N<sub>2</sub> with those for Sc<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>; clearly they are very similar. Also shown in Table 5 are parameters derived (12, 13) on the assumption that the structure is one of *maximum* volume subject to the constraint that all metal–nonmetal bonds are of constant and equal length. Clearly that assumption is a fairly good first approximation to the structure; as remarked earlier (12) it also sheds light on circumstances in which geometries close to close packing (such as the N arrays in the nitrides and the metal arrays in the oxides) might arise.

**TABLE 5**  
Comparison of Free Parameters of Bixbyites and Antibixbyites

	Sc <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	Mg <sub>3</sub> N <sub>2</sub>	Zn <sub>3</sub> N <sub>2</sub>	V <sub>max</sub>
x	0.965	0.968	0.970	0.978	0.973
x	0.392	0.391	0.389	0.398	0.393
y	0.155	0.152	0.152	0.150	0.145
z	0.382	0.380	0.382	0.376	0.381

*Note.* The oxide structure parameters are weighted averages of six or seven independent determinations. The nitrides are from this work and V<sub>max</sub> refers to values for constrained maximum volume (see text).

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