

Study of Ammonolysis Reactions with *in Situ* X-Ray Diffraction: Detection and Crystal Structure of $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$

S. Kaskel,* D. Hohlwein,^{†,1} and J. Strähle*,²

*Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany, and [†]Institut für Kristallographie, Universität Tübingen, Charlottenstrasse 33, D-72070 Tübingen, Germany

Received September 4, 1997; in revised form January 20, 1998; accepted January 27, 1998

DEDICATED TO PROFESSOR H. BÄRNIGHAUSEN ON THE OCCASION OF HIS 65TH BIRTHDAY.

The new ternary nitride $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$ was found by an *in situ* X-ray diffraction study of the ammonolysis of a LiF– WO_3 mixture. The ammonolysis proceeds via $\text{Li}_6\text{W}_2\text{O}_9$ to LiWN_2 , which subsequently decomposes at 900°C to form $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$. For a larger scale synthesis of $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$, the ammonolysis of a mixture of Li_2CO_3 and WO_3 was performed at 900°C. $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$ crystallizes in the anti-TiP type structure with the space group $P6_3/mmc$ and $a = 2.8809(1)$ Å, $c = 10.3456(4)$ Å, and $Z = 2$ as determined from simultaneous Rietveld refinement of X-ray and neutron powder diffraction data. The refinement converged with $R(F^2) = 7.0\%$ for the X-ray data and 8.3% for the neutron data with a total reduced $\chi^2 = 3.54$. The structure consists of alternating layers of WN_6 trigonal prisms and MN_6 octahedra ($M = \text{W}, \text{Li}$), with distances $W-N = 2.11$ Å. © 1998

Academic Press

INTRODUCTION

In recent years, new ternary nitrides $MM'\text{N}_2$ ($M = \text{Li}, \text{Fe}, \text{Mn}, \text{Cr}$; $M' = \text{Mo}, \text{W}$) have been synthesized by the ammonolysis of the ternary oxides or metalloorganic precursors (1–6). Their structures are built up from alternating layers of MN_6 octahedra and $M'\text{N}_6$ trigonal prisms. Three stacking variants are observed in which the nitrogen atoms form close-packed layers (Fig. 1). The anti-TiP type structure, like FeWN_2 (3) and $\text{Fe}_{0.8}M_{1.2}\text{N}_2$ ($M = \text{Mo}, \text{W}$) (5, 6), shows an AABB stacking. The structures of the iron compounds differ, however, from the anti-TiP type in an alternative occupation of the trigonal-prismatic holes, resulting in face sharing of WN_6 prisms and FeN_6 octahedra along the c -axis in FeWN_2 and $\text{Fe}_{0.8}M_{1.2}\text{N}_2$ ($M = \text{Mo}, \text{W}$), whereas in the anti-TiP type structure, exclusively edge-sharing

polyhedra are found. A third variant was observed for LiMoN_2 (1). It shows an AABCC stacking with edge- and face-sharing metal-centered polyhedra.

Our investigation of the reaction of a mixture of LiF and WO_3 (1 : 1) with NH_3 gas shows that at 600°C $\text{Li}_6\text{W}_2\text{O}_9$ is obtained, which at 700°C is transformed to LiWN_2 (2). At 900°C the latter decomposes to afford $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$. The hitherto unknown $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$ was then synthesized in larger scale by ammonolysis of a Li_2CO_3 – WO_3 mixture (0.4 : 1). It crystallizes in the anti-TiP type structure, whereas LiWN_2 is assumed to be isostructural with LiMoN_2 (1, 2).

EXPERIMENTAL

Chemical Synthesis

A 0.4 : 1 mixture of Li_2CO_3 (99% p.a., Merck) and WO_3 (99.9%, Fluka) was ground in a mortar and placed in an alumina boat. To protect the silica tube used for the ammonolysis reaction from small amounts of subliming lithium compounds, an additional inner corundum tube was inserted. The mixture was heated under flowing ammonia gas (> 99%, BASF) to 900°C at a rate of 50°C/h and the temperature was maintained for 15 h. The ammonia was purified by passing it through a column with active carbon and then through a column with KOH pellets. After the sample was cooled to room temperature (2 h) and ground, the reaction was completed by heating the sample for another 15 h at 900°C in the same apparatus. The product is a gray-black air-stable powder, which is only attacked by hot aqua regia to give a WO_3 suspension after about 0.5 h. The purity of the phase was controlled by X-ray diffraction.

Elemental Analysis

Nitrogen was determined by combustion analysis with a Carlo Erba 1104 analyzer. The low value of 9.6% (calcd.

¹ Permanent address: Hahn-Meitner-Institut, Glienicke Str. 100, D-14109 Berlin, Germany.

² To whom correspondence should be addressed. E-mail: joachim.straehle@uni-tuebingen.de.

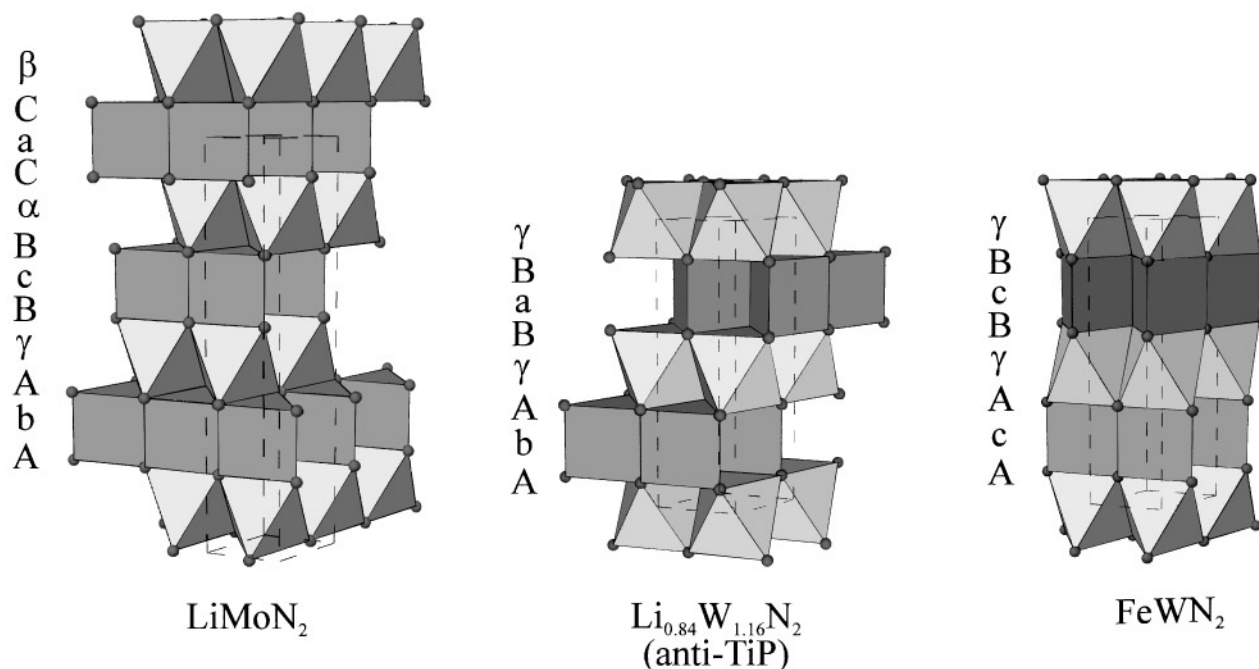


FIG. 1. Structures of LiMoN_2 , $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$ (anti-TiP), and FeWN_2 .

11.3%) is probably due to incomplete combustion of the nitride.

To determine the lithium and tungsten contents, the sample was heated for 1 h in aqua regia. WO_3 was then dissolved by adding solid NaOH pellets. The lithium content was analyzed from this solution by flame emission spectroscopy with a Varian SpectrAA20 analyzer ($\lambda = 670.8$ nm) using Li_2CO_3 as standard. The tungsten content was determined by gravimetric analysis (7) using WO_3 as standard.

Thermogravimetric Analysis

The oxide contamination of the material was estimated by TGA measurements on a NETSCH STA 409 analyzer. The sample was heated to 980°C at a rate of $5^\circ\text{C}/\text{min}$ under an atmosphere of oxygen. The combustion of the nitride was complete at 700°C since the weight of the sample did not further change. The total mass gain was 13.9% as expected for the proposed composition, if Li_2O and WO_3 are assumed to be the products of the thermolysis.

Magnetic Susceptibility and Electrical Conductivity

The magnetic susceptibility was measured at a constant magnetic field of 20,000 G with a Quantum Design SQUID magnetometer in a gelatin capsule. The diamagnetic contribution of the capsule was subtracted but no further correction of the data was made.

The electrical conductivity of a pellet made from the pulverized compound was measured at room temperature using a four-point method.

Structure Determination

X-ray powder diffraction data were collected in transmission geometry on a Siemens D5000 diffractometer ($2\theta = 10\text{--}110^\circ$) with $\text{CuK}\alpha$ radiation using a germanium incident beam monochromator. The pattern was indexed using DICVOL (8), yielding an initial hexagonal setting with lattice constants $a = 2.8820(4)$ and $c = 10.333(2)$ Å. Systematic absences indicated the space group $P31c$, $P\bar{3}1c$, $P6_3mc$, $P\bar{6}2c$, or $P6_3/mmc$. Integrated intensities were extracted from the pattern using FULLPROF (9), and the structure model was obtained with direct methods (SHELXS86 (10)) assuming the space group $P6_3/mmc$. The light atom lithium could not be located from the X-ray data but the statistical occupation of site $2a$ by tungsten indicated that lithium ions are also occupying this site.

Neutron diffraction data were collected at the Hahn-Meitner-Institut, Berlin, on the flat-cone and powder diffractometer E2 with $\lambda = 1.22$ Å, in-pile collimation $15'$, in the 2θ range between 5° and 85° . Scattering lengths were used as reported by Sears (11). By simultaneous refinement of X-ray and neutron data using GSAS (12), the lithium position was determined as a minimum in the difference Fourier analysis ($b_{\text{Li}} = -1.90$ fm) of the neutron data. The refinement converged with an $R(F^2)$ of 7.0% for the X-ray

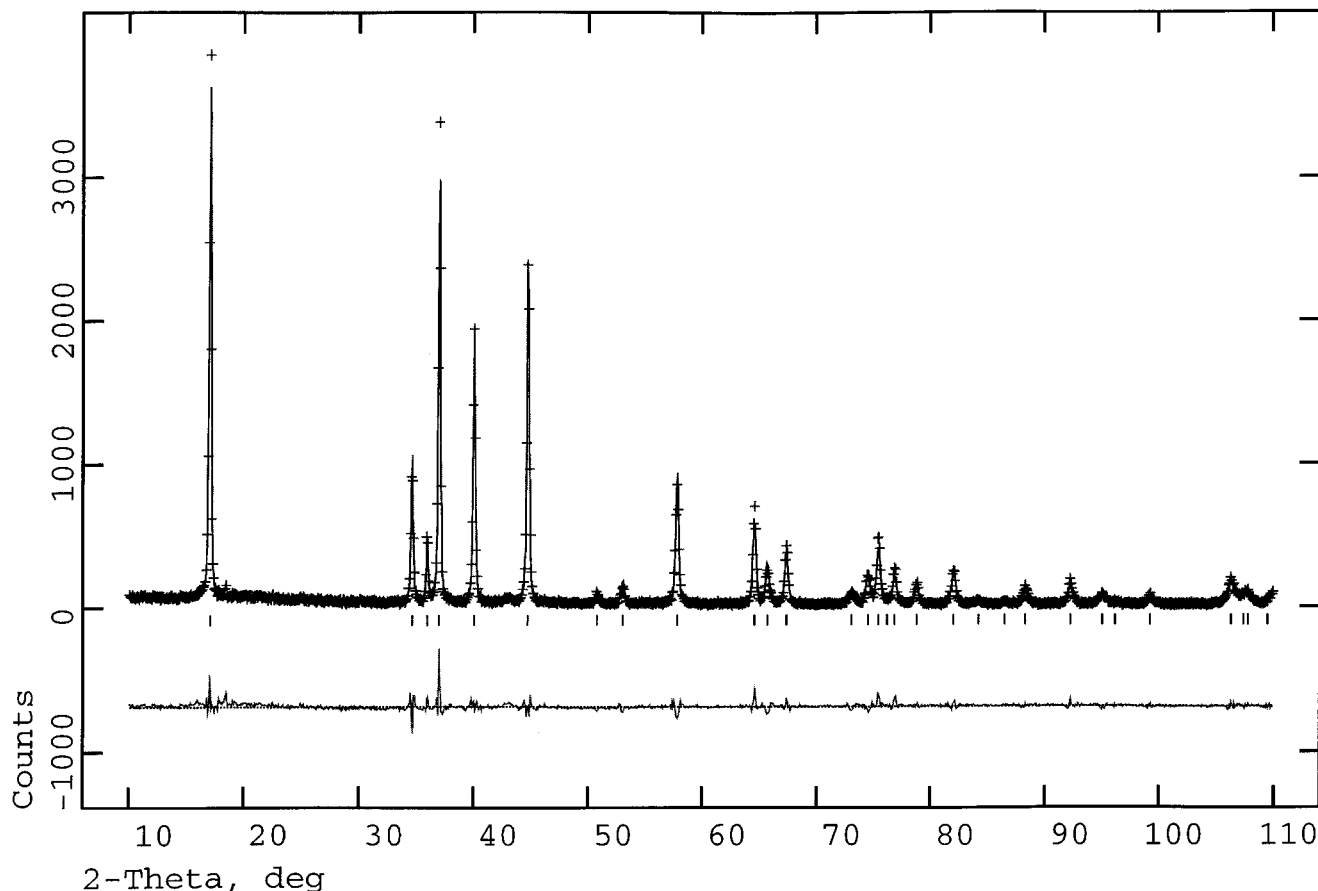


FIG. 2. Rietveld refinement of the X-ray data.

data (Fig. 2) and 8.3% for the neutron data (Fig. 3) with a total reduced χ^2 of 3.54 (Table 1). The thermal parameters of the lithium and tungsten atoms occupying site 2a were constrained to be identical (Table 2).

In Situ Powder Diffraction

In situ experiments were performed with a Siemens D5000 powder diffractometer (θ/θ geometry) equipped with a Bühler HDKS1 high-temperature chamber and a position-sensitive detector (BRAUN). A mixture of LiF and WO_3 (1:1) was placed on a platinum sample holder and heated stepwise at a rate of $2^\circ\text{C}/\text{s}$ under flowing ammonia in intervals of 25°C up to 1200°C . After each interval the temperature was kept constant for 5 min to register the diffraction pattern ($2\theta = 10\text{--}40^\circ$).

RESULTS AND DISCUSSION

The hitherto unknown ternary nitride $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$ was synthesized by heating a mixture of Li_2CO_3 and WO_3 (0.4:1) under flowing ammonia to 900°C for 30 h. When

TABLE 1
Crystal Data and Results of the Rietveld Refinement
for $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$

| | |
|---|--|
| Formula weight | 247.11 |
| Space group | $P6_3/mmc$ |
| Lattice constants (\AA) | $a = 2.8809(1)$ $c = 10.3456(4)$ |
| Volume (\AA^3) | 74.36(1) |
| $D_{\text{calc}}(\text{g}/\text{cm}^3)$ | 11.069 |
| Formula units | $Z = 2$ |
| Color | Gray-black |
| Number of parameters | 30 |
| χ^2 | 3.54 |
| X-ray data | |
| $2\theta_{\text{max}}(\text{deg})$ | 110.0 |
| X-ray radiation | $\text{CuK}\alpha_1$ ($\lambda = 1.5405 \text{\AA}$) |
| Monochromator | Germanium |
| $R_{\text{wp}}/R_{\text{p}}/R_{\text{exp}}$ | 0.178/0.131/0.106 |
| $R(F^2)$ | 0.070 |
| Neutron data | |
| $2\theta_{\text{max}}(\text{deg})$ | 85.0 |
| Neutron radiation (λ) | $\lambda = 1.220 \text{\AA}$ |
| $R_{\text{wp}}/R_{\text{p}}/R_{\text{exp}}$ | 0.058/0.046/0.021 |
| $R(F^2)$ | 0.083 |

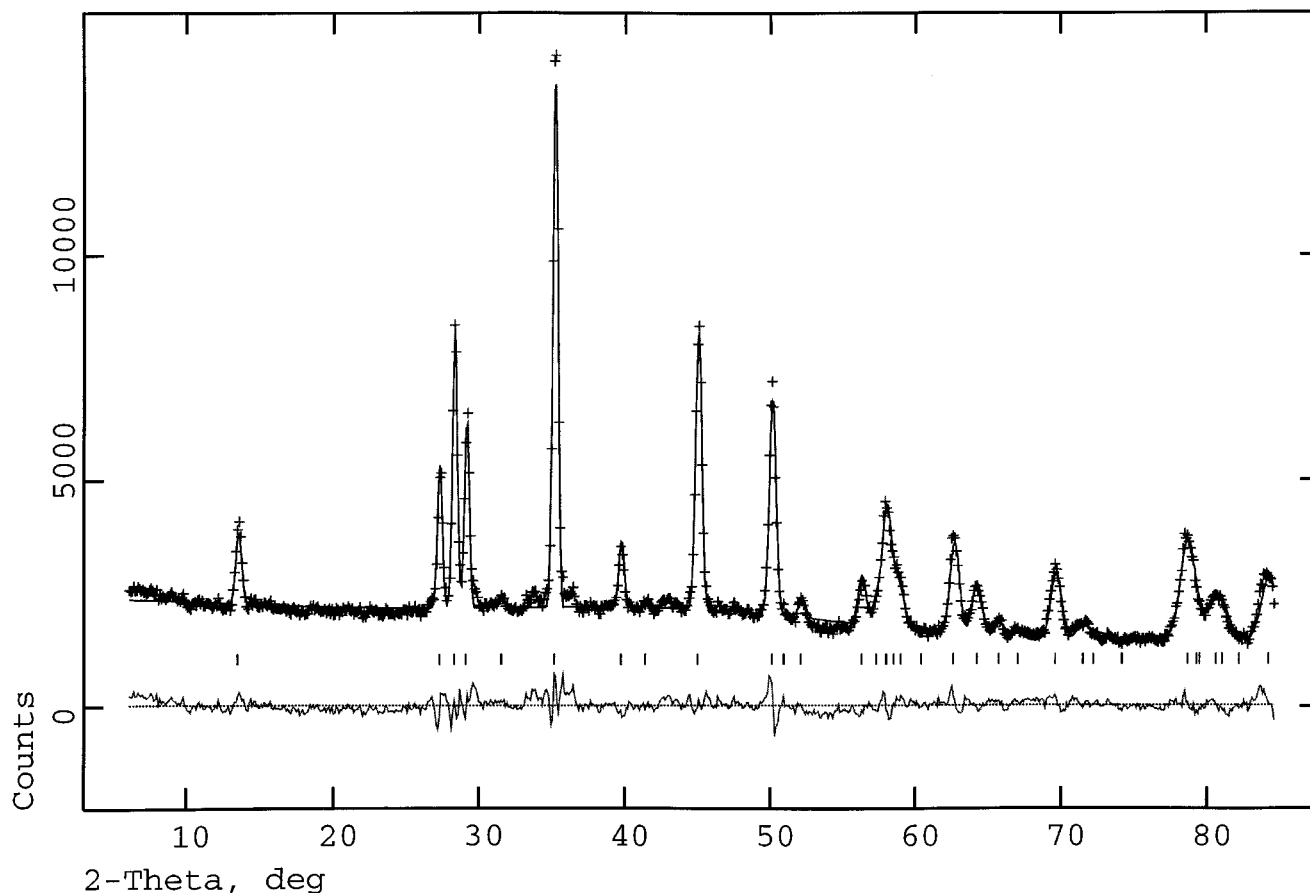
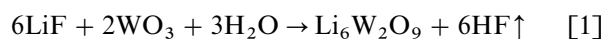


FIG. 3. Rietveld refinement of the neutron data.

higher or lower $\text{Li}_2\text{CO}_3:\text{WO}_3$ ratios were used, impurities were detected by X-ray diffraction. *In situ* powder diffraction shows that the compound is also formed when LiF is used instead of Li_2CO_3 and that it is a product of the decomposition of LiWN_2 under ammonia. A separate synthesis of the oxide precursors Li_2MO_4 used in the synthesis of LiMN_2 ($M = \text{Mo}, \text{W}$) (1, 2) is therefore not necessary.

The reaction of the LiF- WO_3 mixture (1:1) with gaseous ammonia proceeds via several steps (Fig. 4). Below 600°C three modifications of WO_3 (13–15) are identified in

addition to LiF. Since WO_3 does not show these structural changes when heated in vacuo, they are possibly due to partial reduction or doping by nitrogen. At 600°C $\text{Li}_6\text{W}_2\text{O}_9$ (16) is formed, which at 700°C transforms to LiWN_2 to finally yield $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$ at about 900°C . The formation of $\text{Li}_6\text{W}_2\text{O}_9$ at 600°C presumably results from a reaction with H_2O , which is formed by the beginning ammonolysis reaction (Eq. [1]).



The mechanism of the ammonolysis reaction is similar to that observed by DiSalvo *et al.* (1) for the synthesis of LiMoN_2 . They also reported a lithium-rich oxide intermediate, Li_4MoO_5 , but no ternary nitride except LiMoN_2 was found.

Our preliminary investigations, however, indicate that an anti-TiP type lithium molybdenum nitride with composition similar to that observed for $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$ can also be prepared by the reaction of $\text{Li}_2\text{CO}_3\text{-MoO}_3$ mixtures with gaseous ammonia.

TABLE 2
Atomic Parameters of $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$

| Atom | Site | x | y | z | Occupancy | $U_{\text{iso}} \times 100 (\text{\AA}^2)$ |
|------|------|---------------|---------------|---------------|-----------|--|
| W(1) | 2c | $\frac{1}{3}$ | $\frac{2}{3}$ | $\frac{1}{4}$ | 1 | 1.29(4) |
| W(2) | 2a | 0 | 0 | 0 | 0.162(3) | 1.2(2) |
| Li | 2a | 0 | 0 | 0 | 0.89(5) | 1.2(2) |
| N | 4f | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.6253(2) | 1 | 0.61(5) |

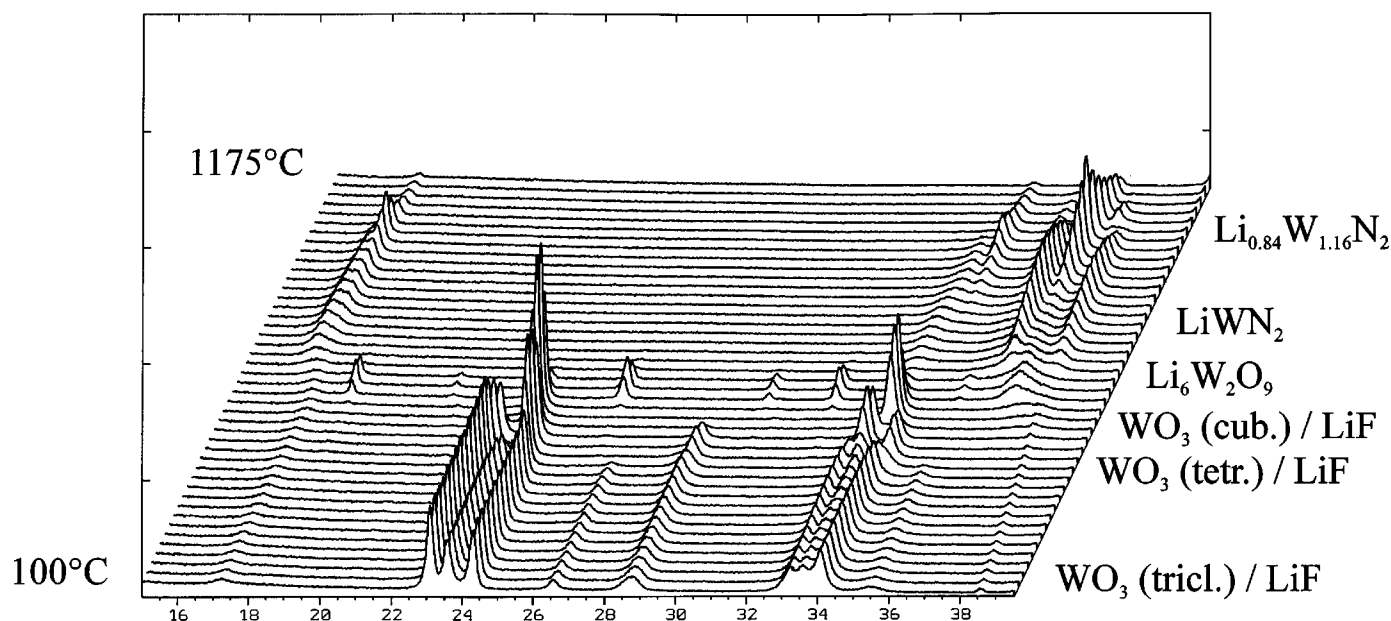


FIG. 4. *In situ* X-ray diffraction diagrams of the ammonolysis of a LiF-WO₃ mixture between 100 and 1175°C in steps of 25°C.

Li_{0.84}W_{1.16}N₂ crystallizes in the anti-TiP type structure with the space group $P6_3/mmc$ and $a = 2.8809(1)$ and $c = 10.3456(4)$ Å (Table 1). This structure type was also found for MnMoN₂ (3). The structure (Fig. 1) is built up from alternating layers of WN₆ trigonal prisms and MN₆ octahedra ($M = \text{Li}, \text{W}$). The octahedral holes are statistically occupied by tungsten (16%) and lithium (84%), which was shown by simultaneous Rietveld refinement of X-ray and neutron powder diffraction data. This result is in good agreement with the elemental analysis (Table 4).

The structure can be described as a stacking AbA_γBaB_γ of close-packed nitrogen layers with cations in octahedral (γ) and trigonal-prismatic (a, b) holes. Since Li_{0.84}W_{1.16}N₂ is an interstitial nitride, the inverse formulation is also useful

to describe the structure as a close packing of metal atoms $A\beta C\alpha B\alpha C\beta$ with nitrogen atoms in octahedral holes (Fig. 5). In the [001] direction NM₆ octahedra are alternately sharing faces and edges. The structure can therefore be explained as built up from NiAs layers shifted by a shear operation parallel to the a - b plane every second layer of octahedra (Fig. 5). The Li-N and W-N distances (Table 3) of 2.105 and 2.109 Å are similar to those reported for LiMoN₂ (Li-N = 2.179 and 2.098 Å; Mo-N = 2.091 and 2.095 Å), which forms a related structure with a stacking variant AbA_γBcB_zCaC β (Fig. 1). The LiN₆ octahedra in Li_{0.84}W_{1.16}N₂ are slightly distorted. As in the whole family of layered nitrides, metal-metal contacts are short (2.881 Å), indicating strong interactions between the tungsten atoms.

The magnetic susceptibility per mass at 300 K is $\chi_g = -1.4(3) \times 10^{-7}$ emu/g without any correction for the core diamagnetism and $\chi_g = +7(3) \times 10^{-8}$ emu/g if the core diamagnetism is subtracted using standard increments (17).

TABLE 3
Selected Bond Distances and Angles in Li_{0.84}W_{1.16}N₂^a

| Bond distances (Å) | | Bond angles (deg) | |
|--|-----------|---|----------|
| W(1)-W(1) ^I | 2.8809(1) | N ^{II} -W(1)-N ^{III} | 86.4(1) |
| W(2)/Li-W(2) ^I /Li ^I | 2.8809(1) | N ^{II} -W(1)-N ^{IV} | 75.6(1) |
| W(1)-W(2)/Li | 3.0751(1) | N ^{II} -W(1)-N ^V | 133.5(1) |
| W(1)-N ^{II} | 2.105(1) | N ^{II} -W(2)/Li-N ^{III} | 86.2(1) |
| W(2)/Li-N ^{II} | 2.109(1) | N ^{II} -W(2)/Li-N ^{VI} | 93.8(1) |
| N-N ^{VII} | 2.579(3) | N ^{III} -W(2)/Li-N ^{VI} | 180.0(0) |

^aSymmetry codes: I, $x+1, y, z$; II, $1-x, 1-y, z-\frac{1}{2}$; III, $-x, 1-y, z-\frac{1}{2}$; IV, $1-x, 1-y, 1-z$; V, $1-x, 2-y, 1-z$; VI, $x, y-1, \frac{1}{2}-z$; VII, $x, y, \frac{3}{2}-z$.

TABLE 4
Elemental Analysis

| Element | Calculated for Li _{0.84} W _{1.16} N ₂ | Observed |
|---------|--|----------|
| Li | 2.36 | 2.35(3) |
| W | 86.3 | 85.2(8) |
| N | 11.3 | 9.6(4) |

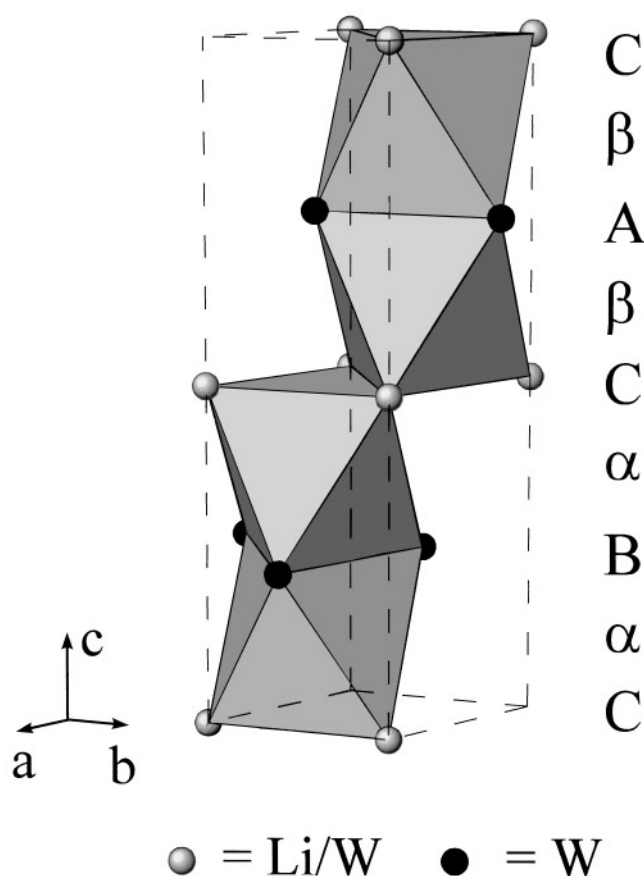


FIG. 5. Stacking of nitrogen-centered NM_6 octahedra ($M = \text{Li}, \text{W}$) in $\text{Li}_{0.84}\text{W}_{1.16}\text{N}_2$.

Measurements between 100 and 300 K show that this weak paramagnetism is temperature independent in the limits of error as expected for an electron-conducting material ($\sigma = 0.7 \Omega^{-1}\text{cm}^{-1}$ at 298 K).

ACKNOWLEDGMENTS

We are grateful to Dr. J. Janek and M. Vennekamp for the measurement of the electrical conductivity and F. Auer for the performance of the flame emission analysis. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

REFERENCES

1. S. H. Elder, L. H. Doerrer, and F. J. DiSalvo, *Chem. Mater.* **4**, 928 (1992).
2. P. Subramanya Herle, M. S. Hegde, N. Y. Vasanthacharya, J. Gopalakrishnan, and G. N. Subbanna, *J. Solid State Chem.* **112**, 208 (1994).
3. D. S. Bem, C. M. Lampe-Önnerud, H. P. Olsen, and H.-C. zur Loye, *Inorg. Chem.* **35**, 581 (1996).
4. K. S. Weil and P. N. Kumata, *J. Solid State Chem.* **128**, 185 (1997).
5. J. D. Houmes, S. Deo, and H.-C. zur Loye, *J. Solid State Chem.* **131**, 374 (1997).
6. D. S. Bem, H. P. Olsen, and H.-C. zur Loye, *Chem. Mater.* **7**, 1824 (1995).
7. A. I. Vogel, "Vogel's Textbook of Quantitative Chemical Analysis," 5th ed. Longman Scientific & Technical, Harlow, 1989.
8. A. Boulitif and D. Louër, *J. Appl. Crystallogr.* **24**, 987 (1991).
9. J. Rodriguez-Carvajal, FULLPROF, Version 3.1, FORTRAN Program for Rietveld Refinements, Laboratoire Leon Brillouin, 1996.
10. G. M. Sheldrick, *Acta Crystallogr., Sect. A* **46**, 467 (1990).
11. V. F. Sears, in "International Tables for X-Ray Crystallography" (A. J. C. Wilson, Ed.), Vol. C. Kluwer, Dordrecht, 1995.
12. A. C. Larson and R. B. Von Dreele, General Structure Analysis System, Los Alamos, 1994.
13. R. Diehl, G. Brandt, and E. Salje, *Acta Crystallogr., Sect. B* **34**, 1105 (1978).
14. W. L. Kehl, R. G. Hay, and D. Wahl, *J. Appl. Phys.* **23**, 212 (1952).
15. O. Yamaguchi, D. Tomihisa, H. Kawabata, and K. Shimizu, *J. Am. Ceram. Soc.* **70**, C94 (1987).
16. M. Parmentier, C. Gleitzer, and J. Aubry, *Compt. Rend. C* **274**, 1681 (1972).
17. A. Weiss and H. Witte, "Magnetochemie." Verlag Chemie, Weinheim, 1973.