

# Crystal Structure of the Oxidenitride, $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$

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Crystals of rhombohedral  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$  (space group  $R\bar{3}(h)$ , No. 148,  $Z = 3$ ,  $a = 5.984(4)$  Å,  $c = 25.484(8)$  Å) were obtained during a study of the Li–Ba–Nb–N system when a mixture of Li, Ba, and Nb confined in quartz was heated at 850°C under flowing  $\text{N}_2$ . Refinement of single crystal data based upon  $F^2$  yielded  $R2 = 0.024$  and  $wR2 = 0.047$ .  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$  crystallizes isotypically with  $\text{Li}_{16}\text{Ta}_2\text{N}_8\text{O}$  in an anti-fluorite type superstructure. The Nb and two of the four independent Li ions are tetrahedrally coordinated by nitrogen anions; the remaining two Li ions are tetrahedrally coordinated by one oxygen and three nitrogen anions. The compound can also be prepared by heating a  $\text{Li}_3\text{N}:\text{Nb}_2\text{O}_5:\text{NbN} = 16/3:1/5:8/5$  molar mixture under flowing Ar/ $\text{N}_2$  at 900°C for 24 h. Magnetic susceptibility data between 10 and 300 K exhibit temperature independent paramagnetism. © 1996 Academic Press, Inc.

## INTRODUCTION

The synthesis, structure, and selected properties of numerous transition metal-containing oxidenitrides prepared by reacting an oxide with either ammonia gas or a metal nitride have been reported recently:  $\text{Na}_3\text{WO}_3\text{N}$  (1),  $\text{SrMo}(\text{O},\text{N})_3$  (2),  $\text{BaCeLn}(\text{O},\text{N})_4$  ( $Ln = \text{La}, \text{Ce}$ ) (3),  $\text{V}_{2.0}\text{Mo}_{1.0}\text{O}_{1.7}\text{N}_{2.4}$  (4),  $\text{La}_2\text{AO}_3\text{N}$  ( $A = \text{V}, \text{Nb}, \text{Ti}, \text{Al}$ ) (5),  $\text{Li}_{2-x}\text{Nb}_{2+x}\text{O}_y\text{N}_{4-y}$  ( $0 \leq x \leq 0.31$ ;  $0.46 \leq y \leq 1.46$ ) and related phases (6), and  $\text{Ln}_2\text{Ta}_2\text{O}_5\text{N}_2$  ( $Ln = \text{Nd}–\text{Yb}, \text{Y}$ ) (7). Several other oxidenitrides synthesized by diverse methods,  $\text{Na}_4\text{MO}_2\text{N}_2$  ( $M = \text{Mo}, \text{W}$ ) (8),  $\text{Na}_5\text{WO}_4\text{N}$  (9),  $\text{Li}_{16}\text{Ta}_2\text{N}_8\text{O}$  (10), and  $\text{K}_6\text{W}_2\text{N}_4\text{O}_3$  (11), have also been characterized structurally.

During our studies of the quaternary nitrides  $\text{Li}_3\text{Ba}_2\text{MN}_4$  ( $M = \text{Nb}, \text{Ta}$ ) (12) we identified in the Nb system the phase  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$  which we later found to be isostructural with  $\text{Li}_{16}\text{Ta}_2\text{N}_8\text{O}$  (10). We report the synthesis, structure, and magnetic susceptibility of  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$ .

## EXPERIMENTAL

**Synthesis.** Single crystals of  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$  were originally obtained when a mixture in the molar ratio Li:Ba

(99.7%, Cerac, Inc.): Nb (99%, E. H. Sargent & Co., 80 mesh) = 2:1:1, confined in a Nb boat which was placed in a quartz reaction tube, was heated under flowing Ar (AGA Gas, Inc.) to 850°C at a rate of 97°C/h, held at 850°C under flowing nitrogen (AGA Gas, Inc.) for 24 h, and then cooled to 150°C at 10.8°C/h under Ar. Colorless transparent single crystals of  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$  were isolated from the air and moisture sensitive crushed product. Both the Ar and  $\text{N}_2$  gases were purified by molecular sieves (4–8 mesh, Aldrich) and De-Ox catalyst (Johnson Matthey). The oxygen in the compound probably came from moisture that adhered to the quartz reaction tube.

Samples of  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$  for X-ray powder diffraction and magnetic susceptibility measurements were prepared by heating a mixture of the molar ratio  $\text{Li}_3\text{N}:\text{Nb}_2\text{O}_5$  (Apache Chemicals, 99.9%): NbN = 16/3:1/5:8/5. The mixture, confined in a Nb boat which was then placed in a quartz reaction tube, was heated from room temperature to 900°C within 2 h under flowing Ar/ $\text{N}_2$ , kept at 900°C for 24 h, and then quenched. The light yellow, air-sensitive powder was almost phase-pure based on the X-ray powder diffraction pattern (see Fig. 4). The reactant  $\text{Li}_3\text{N}$  was prepared by heating Li metal under flowing  $\text{N}_2$  at 450°C for 36 h. NbN was prepared by heating  $\text{NbCl}_5$  (Johnson Matthey, grade 1) under flowing  $\text{NH}_3$  at 700°C for 5 h.

**X-ray diffraction.** Powder X-ray diffraction data were collected with both a 114.6 mm Guinier camera (internal standard: Si) and a Philips APD diffraction system with copper  $K\alpha$  radiation. The powder diffractometer data were stripped of the  $K\alpha_2$  component with the APD software, corrected for the  $\theta$ -compensating slit as described previously (13), and plotted with the program GRAPHOR (14). The program LAZY PULVERIX (15) was used for powder intensity calculations. Single crystal diffraction data were collected on a Rigaku AFC6S 4-circle diffractometer with graphite monochromated  $\text{MoK}\alpha$  radiation.

**Structure determination.** Lattice parameters of the irregularly shaped transparent colorless crystal mounted on a glass fiber were obtained from a least-squares refinement of the setting angles of 16 carefully centered reflections in the range  $37.89^\circ < 2\theta < 39.28^\circ$ . Based on the systematic

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TABLE 1  
Summary of Crystal and Diffraction Data  
for  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$

Chemical formula	$\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$
Formula weight	424.92
Space group	$R\bar{3}$ ( <i>h</i> ) (No. 148)
<i>a</i> , <i>c</i> (Å)	5.984(4), 25.484(8)
<i>V</i> (Å <sup>3</sup> )	790.1(8)
<i>Z</i>	3
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	2.678
<i>T</i> (°C)	-100 ± 1
Crystal color, Habit	colorless, irregular
Crystal dimensions (mm)	0.080 × 0.120 × 0.150
2θ max (deg)	60.0
Scan type	$\omega - 2\theta$
X-ray radiation (λ)	$\text{MoK}\alpha$ (λ = 0.71069 Å)
Monochromator	Graphite
Octants collected	<i>hkl</i> ; - <i>h</i> - <i>kl</i>
Absorption coeff $\mu$ (cm <sup>-1</sup> )	20.67
Measured reflections	2224
Observed reflections <sup>a</sup>	508
Unique reflections	509
<i>F</i> 000	582
No. of variables	43
Max (min) peak in final diff. map	0.74 (-0.69) e <sup>-</sup> /Å <sup>3</sup>
Goodness of fit	1.03
<i>R</i> 2 <sup>b</sup> , <i>wR</i> 2 <sup>c</sup>	0.024, 0.047

<sup>a</sup>  $I > 0.00\sigma(I)$ ; one reflection had negative intensity.

<sup>b</sup>  $R2 = \sum |F_o^2 - F_c^2| / \sum F_o^2$ .

<sup>c</sup>  $wR2 = [\sum w(|F_o^2 - F_c^2|)^2 / \sum (wF_o^2)^2]^{1/2}$ .

absences of *hkl*: -*h* + *k* + *l* ≠ 3*n*, the successful solution, and the refinement of the structure, the space group was determined to be  $R\bar{3}$  (No. 148). [To help substantiate that the space group chosen was correct, refinements were also effected in space groups  $R\bar{3}m$ ,  $R3m$ , and  $R32$ . In all of these refinements problems arose, e.g., the Nb atom temperature factor becoming nonpositive or high *R* values.]

Data were collected at -100°C by the  $\omega - 2\theta$  scan

TABLE 2  
Atomic Positions and *B*(eq) for  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (eq)(Å <sup>2</sup> ) <sup>a</sup>
Nb	0	0	0.24944(1)	0.27(1)
N(1)	0.3089(4)	0.3110(4)	0.22491(7)	0.47(5)
N(2)	0	0	0.3265(1)	0.50(7)
O	0	0	0	0.5(1)
Li(1)	0.357(1)	0.303(1)	0.4747(1)	0.8(1)
Li(2)	0.032(1)	0.340(1)	0.0233(2)	0.9(1)
Li(3)	0	0	0.0769(3)	0.7(2)
Li(4)	0	0	0.4165(3)	1.0(2)

<sup>a</sup> The equivalent isotropic temperature factor is defined as (25)  
 $B(\text{eq}) = 8\pi^2/3 [\sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j]$ .

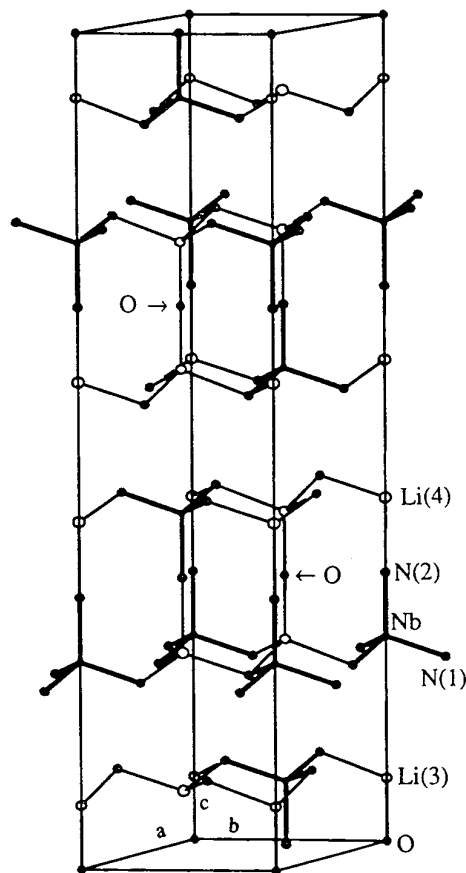


FIG. 1. Unit cell of  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$  with Li(1) and Li(2) omitted for clarity. The thicker bonds denote  $\text{NbN}_4$  tetrahedra.

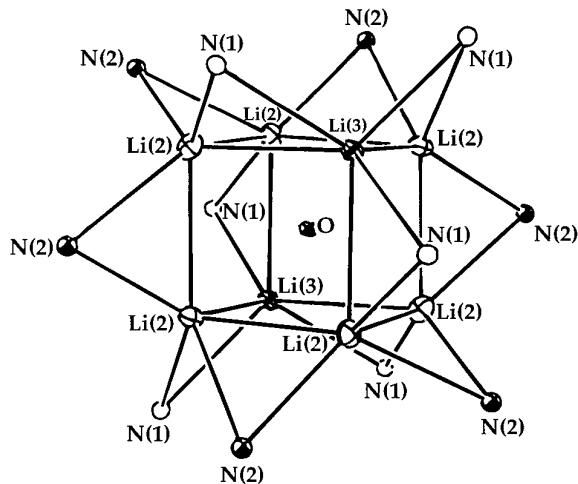


FIG. 2. Oxygen atom coordination environment. The first coordination sphere is composed of six Li(2) and two Li(3) atoms in a distorted cubic arrangement. Six N(1) and six N(2) atoms comprise the second coordination sphere.

TABLE 3  
Anisotropic Thermal Parameters,  $U_{ij}$ , for  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}^a$

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Nb	0.0034(1)	0.0034	0.0034(2)	0.0017	0	0
N(1)	0.0064(9)	0.0060(9)	0.0054(7)	0.0031(8)	0.0007(7)	0.0003(7)
N(2)	0.007(1)	0.007	0.005(2)	0.003	0	0
O	0.006(1)	0.006	0.006(2)	0.003	0	0
Li(1)	0.012(2)	0.010(2)	0.010(2)	0.006(2)	0.001(1)	-0.000(1)
Li(2)	0.012(2)	0.012(2)	0.012(2)	0.007(2)	0.003(1)	-0.001(1)
Li(3)	0.010(2)	0.010	0.007(4)	0.005	0	0
Li(4)	0.013(2)	0.013	0.011(3)	0.007	0	0

<sup>a</sup> The anisotropic temperature factor coefficients  $U_{ij}$  are defined as  $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$ .

technique to a maximum  $2\theta$  value of  $60.0^\circ$ . Of the 2224 reflections which were collected, 509 were unique; equivalent reflections were merged ( $R_{\text{int}} = 0.036$ ). The intensities of three representative reflections measured after every 150 reflections declined by 0.60%; a linear correction factor was applied to compensate for this intensity decrease. An

empirical absorption correction applied by using the linear absorption coefficient for  $\text{MoK}\alpha$  radiation,  $20.7 \text{ cm}^{-1}$ , resulted in transmission factors that ranged from 0.91 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient =  $0.44(8) \times 10^{-6}$ ).

TABLE 4  
Selected Bond Distances (Å) and Angles (deg) in  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$

Bond	Distances	Bond	Angles
Nb–N(1)	1.957(2) (3×)	N(1)–Nb–N(1)	110.31(5) (3×)
Nb–N(2)	1.964(4)	N(1)–Nb–N(2)	108.62(5) (3×)
Li(1)–N(1)	{ 2.164(5) 2.135(4) 2.066(6) 2.324(7)	N(1)–Li(1)–N(1)	{ 91.4(2) 116.5(3) 109.9(2) 108.5(2)
Li(2)–N(1)	2.192(5)		{ 108.2(3) 118.6(3)
Li(3)–N(1)	2.227(3)		{ 92.7(2) 116.2(2)
Li(4)–N(1)	2.157(3)	N(1)–Li(2)–N(2)	{ 109.8(3) 109.7(2)
Li(2)–N(2)	{ 2.033(4) (3×) 2.209(7) (3×)	N(2)–Li(2)–N(2)	{ 109.2(2) 109.7(2)
Li(4)–N(2)	2.295(8)	N(1)–Li(2)–O	{ 109.2(2) 116.6(3)
Li(2)–O	2.034(6) (6×)	N(2)–Li(2)–O	{ 107.7(2) (3×) 111.1(2) (3×)
Li(3)–O	1.959(7)		{ 111.5(2) (3×) 107.3(2) (3×)
Li(1)–Li(1)	{ 2.376(5) (2×) 2.469(8)	N(1)–Li(3)–N(1)	{ 77.2(1) 81.2(2) 106.1(2) 173.2(2)
Li(1)–Li(3)	2.414(7)	N(1)–Li(3)–O	{ 79.6(2) 111.4(1) 114.1(1)
Li(1)–Li(4)	2.487(6)	N(1)–Li(4)–N(1)	{ 79.1(1) (3×) 112.2(1) (3×)
Li(1)–Li(4)	2.487(6)	N(1)–Li(4)–N(2)	{ 180.0 64.2(2)–172.7(3) (21×)
Li(2)–Li(2)	{ 2.279(7) (2×) 2.44(1)		{ 64.9(3)–168.4(2) (21×)
Li(2)–Li(3)	2.376(7)	Nb–N(1)–Li(1)	{ 68.2(1)–180.00 (28×)
Li(2)–Li(4)	2.423(6)	Nb–N(1)–Li(2)	
		Nb–N(1)–Li(3)	
		Nb–N(1)–Li(4)	
		Nb–N(2)–Li(2)	
		Nb–N(2)–Li(4)	
		Li–N(1)–Li	
		Li–N(2)–Li	
		Li–O–Li	

TABLE 5  
Miller Indices and Observed and Calculated  $d$  Spacings and  
Intensities for  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$

$h$	$k$	$l$	$d_o$	$d_c$	$I_o^*$	$I_c$
0	1	2	4.8063	4.8005	100	100
0	0	6	4.2544	4.2473	30	24
1	0	4	4.0251	4.0202	70	72
			3.7313		11	
1	1	0	2.9902	2.9920	38	31
0	0	9	2.8210	{2.8316	22	4
1	1	-3		{2.8221		12
0	1	8	2.7147	2.7138	19	23
2	0	2	2.5377	2.5392	19	18
1	1	$\pm 6$	2.4451	2.4460	33	11/16
0	2	4	2.3992	2.4002	16	17
1	0	10	2.2877	2.2869	10	14
0	0	12	2.1237	2.1237	6	5
2	0	8	2.0097	2.0101	6	7
2	1	-2	1.9345	{1.9360	15	10
1	2	2		{1.9360		6
2	1	4	1.8709	{1.8722	15	6
1	2	-4		{1.8722		10
0	2	10	1.8165	1.8169	5	5
1	1	$\pm 12$	1.7313	1.7318	28	5/23
3	0	0	1.7256	1.7274	31	22
0	1	14	1.7175	1.7174	13	5
1	2	8	1.6676	{1.6685	7	4
2	1	-8		{1.6685		5
0	3	6	1.5990	{1.6002	10	4
3	0	6		{1.6002		4
1	2	-10	1.5520	{1.5530	5	4
2	1	10		{1.5530		3
1	0	16	1.5232	1.5225	4	4
2	2	0	1.4945	1.4960	4	4
2	0	14	1.4892	1.4895	3	4
3	0	9	1.4722	{1.4747	3	<1
0	3	9		{1.4747		<1
2	2	3		{1.4733		<1
3	1	2	1.4270	{1.4283	5	4
1	3	-2		{1.4283		2
2	2	$\pm 6$	1.4098	1.4110	5	2/3
3	1	4	1.4008	{1.4021	5	2
1	3	4		{1.4021		4
0	2	16	1.3569	1.3569	3	4
0	3	12	1.3393	{1.3401	6	3
3	0	12		{1.3401		3
2	1	-14	1.3332	{1.3334	4	3
1	2	14		{1.3334		3
3	1	8	1.3093	{1.3101	3	3
1	3	-8		{1.3101		2
0	4	2	1.2879	1.2889	2	2
1	1	$\pm 18$	1.2795	1.2797	3	2/2

The structure was solved by direct methods with the program SHELXS86 (16). Neutral atom scattering factors were taken from Cromer and Waber (17). Calculations were performed by using the TEXSAN (18) crystallographic software package. All atoms were refined aniso-

tropically with the refinement based upon  $F^2$ . The final cycle of full-matrix least-squares refinement (19), based on 508 observed reflections with ( $I > 0.00\sigma(I)$ ) and 43 variable parameters, converged with  $R2 = 0.024$  and  $wR2 = 0.047$ . The crystallographic data, atomic positions,  $U_{ij}$  values,

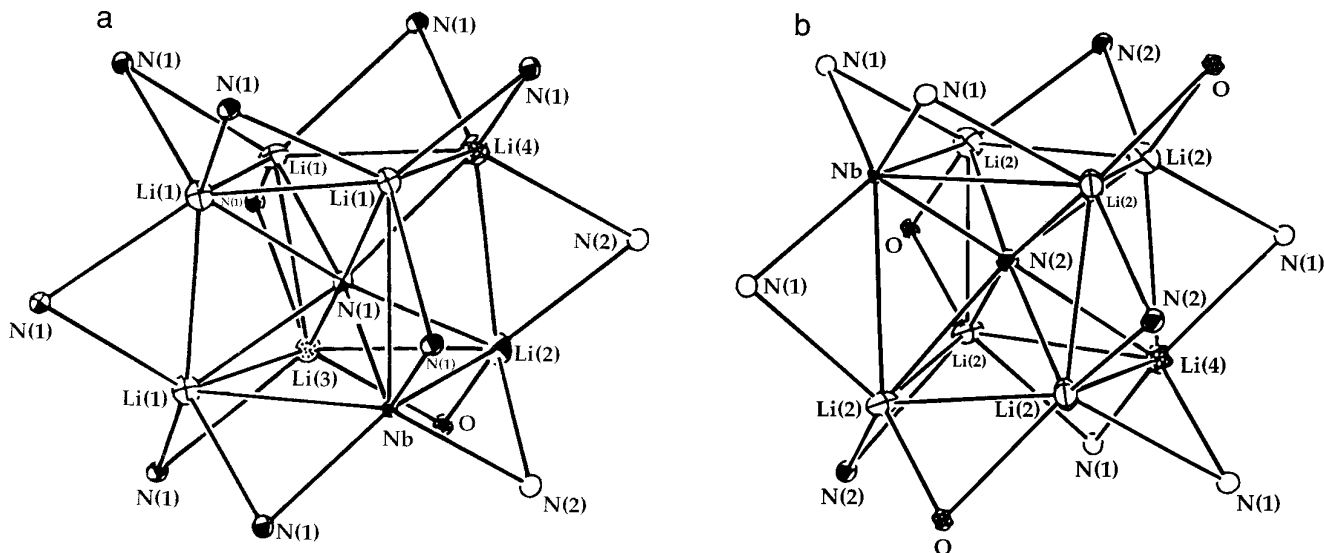


FIG. 3. (a) Nitrogen atom coordination environments. Atom N(1) is coordinated first by eight atoms that occupy the corners of a distorted cube (four Li(1), one Li(2), one Li(3), one Li(4), and one Nb atom) and then by twelve anions, (one O, nine N(1), and two N(2) atoms). (b) Eight atoms also provide distorted cubic coordination for atom N(2): one Nb, one Li(4), and six Li(2) atoms. Six N(1), three N(2), and three O atoms comprise the second coordination sphere.

bond distances, and observed and calculated power patterns are shown in Tables 1–5, respectively.<sup>1</sup>

**Magnetic susceptibility.** Data were measured with a Quantum Design SQUID magnetometer at temperatures between 2 and 300 K. At each temperature magnetic susceptibilities were also measured at various magnetic fields between 200 and 800 G and extrapolated to zero reciprocal field to eliminate ferromagnetic impurity contributions.

## RESULTS AND DISCUSSION

Although the single crystals are colorless, the powder is light yellow. The air and moisture sensitive compound crystallizes isotypically to  $\text{Li}_{16}\text{Ta}_2\text{N}_8\text{O}$  (10). Figure 1 shows the unit cell with the Li(1) and Li(2) atoms omitted for clarity. The unit cell corners are occupied by one O atom; the remaining two O atoms are indicated by arrows. The Nb atoms are tetrahedrally coordinated by N atoms. The Nb–N bonds are darkened in the figure to facilitate viewing. The average Nb–N distance of 1.960 Å is close to the

average Nb–N distance of 1.95 Å in  $\text{Li}_3\text{Ba}_2\text{NbN}_4$  (12) and in  $\text{Li}_7\text{NbN}_4$  (20).

The four independent Li atoms are tetrahedrally coordinated by either N atoms only (Li(1) and Li(4)) or by both N and O atoms (Li(2) and Li(3)) with an average Li–N distance of 2.18 Å and an average Li–O distance of 2.00 Å, the same as those reported for comparable atoms in  $\text{Li}_{16}\text{Ta}_2\text{N}_8\text{O}$  (10).

As shown in Figs. 2 and 3, the coordination environments for O, N(1), and N(2) indicate that  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$  is a superstructure of the antifluorite type. In Fig. 2 it can be seen that the O atom is coordinated by 8  $\text{Li}^+$  cations in the

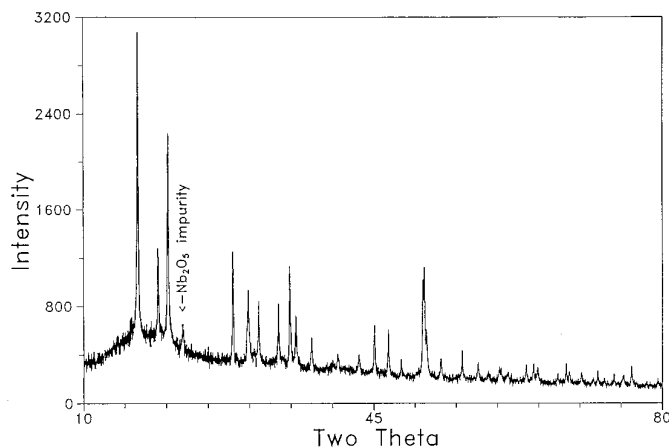


FIG. 4. X-ray powder diffraction pattern for  $\text{Li}_{16}\text{Nb}_2\text{N}_8\text{O}$ .

<sup>1</sup> See NAPS document No. 05344 for 7 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$3.00 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling for the first 20 pages, and \$1.00 for additional 10 pages of material, \$1.50 for postage of any microfiche order.

first coordination sphere and 12  $N^{3-}$  anions in the second coordination sphere with all cations occupying tetrahedral holes formed by the anions. The same situation prevails for the Ca atoms in the fluorite structure.

The coordination environments shown in Fig. 3 for N(1) and N(2) are similar to that of O. All are coordinated by 8 cations in the first coordination sphere and 12 anions in the second coordination sphere with the cations occupying the tetrahedral holes formed by the anions. The N and O atoms form a (distorted) face-centered cubic structure and the Li and Nb atoms occupy tetrahedral holes—an anti-fluorite-type superstructure.

Many Li-containing ternary nitrides have an anti-fluorite superstructure:  $Li_7MN_4$  ( $M = V$  and Mn (21), Nb (20), Ta (22)) and  $Li_6MN_4$  ( $M = Cr, Mo, W$ ) (23). The tendency of the small  $Li^+$  ion to occupy tetrahedral holes formed by  $N^{3-}$  ions is probably the main reason why these compounds form the anti-fluorite type superstructure.

The X-ray powder diffraction pattern of  $Li_{16}Nb_2N_8O$  is shown in Fig. 4. The one very weak impurity reflection at  $2\theta \approx 23.68$  can be assigned to  $Nb_2O_5$ . The observed (Philips APD) and calculated  $d$  spacings and intensities are presented in Table 5. The magnetic susceptibility data show almost temperature-independent paramagnetism between 10 and 300 K ( $\chi = 7.95 \times 10^{-4}$  emu/mol) with a small Curie tail below 15 K. Temperature-independent paramagnetism ( $\chi = 1.53 \times 10^{-4}$  emu/mol) was also reported for  $Ba_2NbN_3$  between 20 and 300 K (24).

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