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Synthesis and structure of $Li_3Ba_2TaN_4$

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Abstract

A new quaternary nitride, $Li_3Ba_2TaN_4$, has been synthesized from Li, Ba and Ta metals under flowing N_2 at high temperature. The structure, as determined by single crystal X-ray diffraction techniques, is monoclinic, space group $C2/c$, $Z=4$, with lattice parameters $a=11.294(2)$ Å, $b=5.678(1)$ Å, $c=11.350(2)$ Å, and $\beta=121.407(7)°$. Refinement based upon F^2 yielded $R2=0.052$ and $wR2=0.074$ (for comparison, a refinement based upon F yielded $R1=0.032$). The Ta and one of the two independent Li ions are tetrahedrally coordinated by N anions; the Li tetrahedra are distorted. By sharing edges, the Ta and Li tetrahedra form chains which are linked together by the remaining Li ions to form the three-dimensional structure.

1. Introduction

Transition metal ternary and quaternary nitrides have received an increased level of attention recently and represent new materials with potentially interesting magnetic and electronic properties [1]. Some of the numerous transition metal-containing ternary nitrides that have been reported include Ca_3CrN_3 [2], Ca_3VN_3 [3], M_3FeN_3 ($M\equiv$Ba, Sr) [4], M_3MnN_3 ($M\equiv$Ba, Sr) [5], all of which have trigonal planar $[M^{III}N_3]^{6-}$ anions with either C_{2v} (nitridovanadate(III) and nitridochromate(III)) or D_{3h} symmetries (nitridoferrate(III) and nitridomanganate(III)). Other transition metal-containing nitrides reported recently include Fe_3Mo_3N [6], $FeWN_2$ [7], Ba_3MN_4 ($M\equiv$Mo, W) [8], and Ca_2ZnN_2 [9]. Several Ta-containing ternary nitrides in which Ta is either tetrahedrally or octahedrally coordinated by N atoms have also been reported: M_2TaN_3 ($M\equiv$Ba, Sr) [10], Li_7TaN_4 [11], $ATaN_2$ ($A=$alkali metals) [12], and $CuTaN_2$ [13]. Very few transition metal-containing quaternary nitrides have been reported. A number of those reported involve the Li–M–Ni–N systems, where $M\equiv$Ca, Sr and Ba [14]. In $LiSr_2CoN_2$ [15] and $M_2LiFe_2N_3$ ($M\equiv$Ba, Sr) [16] the $[Co^IN_2]^{5-}$ and $[Fe_2N_3]^{5-}$ anions, respectively, were characterized. We report the synthesis and structure of a new quaternary nitride $Li_3Ba_2TaN_4$.

2. Experimental details

2.1. Synthesis

A 2:1:1 molar ratio mixture of elemental Li, Ba (99.7%, Cerac), and Ta powder (>99.5%, 325 mesh, Fansteel Metallurgical Corporation) was confined in a Ta boat which was then placed in a quartz reaction tube. The mixture was first heated under flowing Ar (AGA Gas, Inc.) to 860 °C at a rate of 91 °C h^{-1}, held at this temperature under flowing nitrogen (AGA Gas, Inc.) for 34 h, and then cooled to 150 °C under Ar at a rate of 11.5 °C h^{-1}. Pale yellow single crystals of $Li_3Ba_2TaN_4$ were isolated from the crushed product which was both air- and moisture-sensitive. Both the Ar and N_2 gases were purified by molecular sieves (4–8 mesh, Aldrich) and De-Ox catalyst (Johnson Matthey). Typical moisture and oxygen contents of the gases were <0.5 p.p.m. and <1 p.p.m., respectively.

2.2. Structure determination

An irregular crystal of approximate dimensions $0.09\times0.10\times0.14$ mm^3 was selected and sealed in a 0.2 mm glass capillary in an N_2-filled glove bag. All measurements were made on a Rigaku AFC6S 4 circle diffractometer with graphite monochromated Mo Kα radiation ($\lambda=0.71069$ Å). Lattice parameters were obtained from a least-squares refinement by using the angle settings of 19 carefully centered reflections in the range $38.60°<2\theta<39.70°$. Based on the systematic absences ($h0l\neq2n$, all off which were checked, and hkl, $h+k\neq2n$, a few of which were checked), packing considerations, and the successful solution and refinement

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TABLE 1. Summary of crystal and diffraction data for $Li_3Ba_2TaN_4$

Chemical formula	$Li_3Ba_2TaN_4$
Formula weight	532.46
Space group	$C2/c$
a, b, c (Å)	11.294(2), 5.678(1), 11.350(2)
β (degree)	121.407(7)
V (Å^3)	621.2(2)
Z	4
D_{calc} (g cm^{-3})	5.692
T (°C)	25±1
Crystal color, Habit	pale yellow, irregular
Crystal dimensions (mm)	0.09×0.10×0.14
2θ max (deg)	80.0
Scan type	ω-2θ
X-ray radiation (λ)	Mo Kα (λ=0.710 69 Å)
Monochromator	Graphite
Octants collected	hkl; hk-l
Absorption coefficient μ (cm^{-1})	298.08
Measured reflections	1830
Unique reflections	1759
Observed reflections[a]	1644
F000	888
No. of variables	48
Max peak in final diff. map (e$^-$ Å^{-3})	3.45; −3.27
$R2$[b], wR[c]	0.052, 0.074

[a] $I > 0.00\sigma(I)$.

[b] $R2 = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$.

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

TABLE 2. Atomic positions and B(eq) for $Li_3Ba_2TaN_4$

Atom	x	y	z	B(eq)
Ta	0	0.11256(7)	0.25	0.24(1)
Ba	0.20933(4)	−0.03379(8)	0.11183(4)	0.64(1)
N(1)	0.1648(6)	−0.090(1)	0.3376(6)	0.8(2)
N(2)	0.0013(7)	0.312(1)	0.1116(7)	1.0(2)
Li(1)	0	−0.362(4)	0.25	2.4(8)
Li(2)	0.385(2)	−0.044(3)	0.459(2)	1.8(5)

The equivalent isotropic temperature factor is defined as [25]:

$$B(\mathrm{eq}) = \frac{8\pi^2}{3}\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*\vec{a}_i\cdot\vec{a}_j$$

of the structure, the space group was determined to be $C2/c$ (#15). Data were collected at 25±1 °C by the ω-2θ scan technique to a maximum 2θ value of 80°. Of the 1830 reflections which were collected, 1759 were unique. The intensities of three representative reflections that were measured after every 150 reflections declined by 0.70%. The linear absorption coefficient for Mo Kα radiation is 298.1 cm^{-1}. An empirical absorption correction, based upon a PSI-scan, was applied and resulted in transmission factors that ranged from 0.76 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = $0.83 \pm 0.02 \times 10^{-6}$).

The structure was solved by direct methods with the programs MITHRIL [17] and DIRDIF [18]. All atoms were refined anisotropically with the refinement based upon F^2. The final cycle of full-matrix least-squares refinement [19], which was based on 1644 observed reflections ($I > 0.00\sigma(I)$) and 48 variable parameters, converged with unweighted and weighted agreement factors of:

$$R2 = \sum|F_o^2 - F_c^2|/\sum F_o^2 = 0.052$$

$$wR2 = [\sum(w|F_o^2 - F_c^2|)^2/\sum(wF_o^2)^2]^{1/2} = 0.074$$

For comparison, a refinement of the overall scale factor on F with the final parameters and 1455 observed reflections ($I > 3\sigma(I)$) led to

$$R1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.032$$

The maximum and minimum peaks on the final difference Fourier map corresponded to 3.45 and −3.27 e Å^{-3}, respectively. The major residue peaks are near to either Ta or Ba atoms and do not indicate any missed atoms.

Neutral atom scattering factors were taken from Cromer and Waber [20]. Anomalous dispersion effects were included in F_c; values for $\Delta f'$ and $\Delta f''$ were from Cromer [21]. All calculations were performed using the TEXSAN [22] crystallographic software package. Data collection and atomic positional parameters are listed in Tables 1 and 2, respectively. Thermal parameters (U_{ij}) are listed in Table 3.

3. Results and discussion

In the crystal structure of $Li_3Ba_2TaN_4$ (Fig. 1), Ta^{5+} and Li(1) ions are tetrahedrally coordinated by N ions. The Li tetrahedra are distorted (see bond lengths below). These Ta and Li tetrahedra are joined by sharing edges to form parallel chains along b. These chains are then linked together by Li(2) ions to form a three-dimensional network. In Ba_2TaN_3 [10] the Ta tetrahedra are connected to each other by sharing one apex. The Ta–N(1) and Ta–N(2) bond lengths in $Li_3Ba_2TaN_4$ are 1.962(6) Å and 1.942(7) Å, respectively, very close to Ta–N bond lengths in Ba_2TaN_3 (1.922, 1.950, 1.966 and 1.988 Å) and in Li_7TaN_4 (1.964 Å). A list of selected bond distances and angles is given in Table 4. The average Ta–N length observed here is equal to the average Nb–N bond lengths found in Li_7NbN_4 [23], where Nb is also tetrahedrally coordinated by N ions. These comparable distances suggest that Nb and Ta should form similar nitrides with the same or similar structure types.

TABLE 3. Anisotropic thermal parameters, U_{ij}, for $Li_3Ba_2TaN_4$

Atom	U11	U22	U33	U12	U13	U23
Ta	0.0026(1)	0.0016(1)	0.0047(1)	0	0.0017(1)	0
Ba	0.0069(2)	0.0079(2)	0.0086(2)	0.0002(1)	0.0035(1)	−0.0006(1)
N(1)	0.006(2)	0.009(3)	0.011(2)	0.004(2)	0.001(2)	0.000(2)
N(2)	0.013(3)	0.013(3)	0.013(3)	−0.006(2)	0.006(2)	0.002(2)
Li(1)	0.02(1)	0.00(1)	0.04(2)	0	0.00(1)	0
Li(2)	0.014(7)	0.011(7)	0.030(9)	−0.001(6)	0.002(6)	−0.011(7)

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

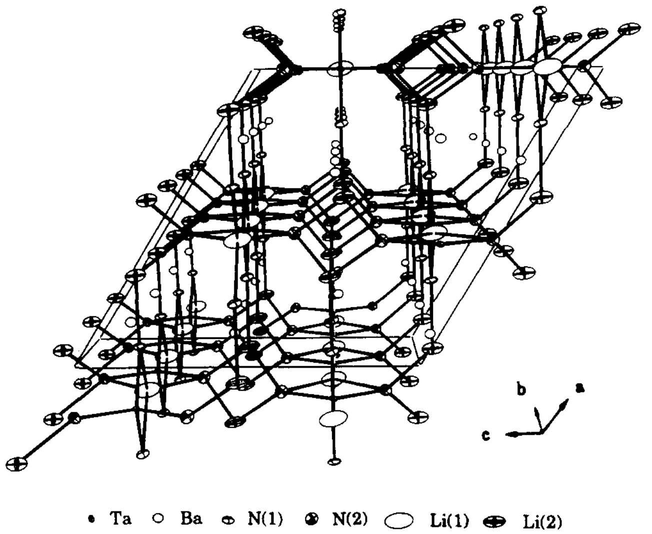


Fig. 1. A view of $Li_3Ba_2TaN_4$ down the *b* axis. The Ta and Li(1) atoms are tetrahedrally coordinated by N atoms. The tetrahedra are joined to form chains that are linked together by Li(2) atoms to form a three-dimensional structure.

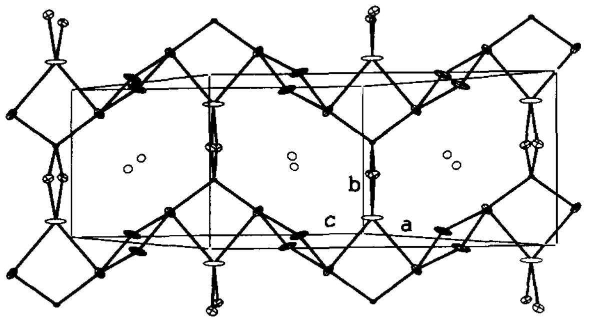
There are two kinds of Li ions in the structure, Li(1) and Li(2). Li(1) ions are tetrahedrally coordinated by N^{3-} ions in a distorted arrangement. The Li(1) and Ta tetrahedra share edges to form Ta–Li(1)–Ta–Li(1)–chains. The Ta–Li(1) chain lies on a twofold axis. The Li(1)–N(1) and Li(1)–N(2) bond lengths are 2.21(2) and 2.43(2) Å, respectively, indicative that the Li tetrahedra are distorted. The Li(2) ions bridge three N^{3-} ions and, therefore, each Li(2) ion links three Ta–Li(1) chains (Fig. 1). The Li(2)–N distances, Li(2)–N(1) at 2.14(2) Å, and Li(2)–N(2) at 2.01(2) and 2.03(2) Å, are comparable to those in Li_3N [24]: 1.938 (twofold coordinated Li) and 2.106 Å (threefold coordinated Li), respectively. If the Li(2)–N(1) bond (perpendicular to the *bc* plane) is not considered, a layered fragment can be viewed in the *bc* plane as shown in Fig. 2.

Figure 2 also shows the positions of the Ba^{2+} ions. Note that one member of each pair of Ba^{2+} ions shown in Fig. 2 is above the layer and the other is below it.

TABLE 4. Selected bond distances (Å) and angles (degrees) in $Li_3Ba_2TaN_4$

Bond distances		Bond angles	
Ta–N(1)	1.962(6)	N–Ta–N av.	109.2(4)
Ta–N(2)	1.942(7)	N(1)–Ba–N(2)	66.2(2)
Li(1)–N(1)	2.21(2)		97.8(2)
Li(1)–N(2)	2.43(2)		127.7(2)
Li(2)–N(1)	2.14(2)	N(1)–Li(1)–N(1)	91.8(9)
Li(2)–N(2) 2x	2.03(2)	N(1)–Li(1)–N(2) av.	122.0(2)
Li(2)–Li(2)	2.32(3)	N(2)–Ba–N(2)	130.9(1)
Ba–N(1)	2.874(7)	N(2)–Li(1)–N(2)	80.8(8)
	2.800(6)	N(1)–Li(2)–N(2)	130.6(9)
	2.968(6)		117.7(8)
Ba–N(2)	3.062(8)	N(2)–Li(2)–N(2)	109.8(8)
	2.881(7)	Ta–N(1)–Li(1)	80.1(5)
	3.257(6)	Ta–N(2)–Li(1)	85.3(4)
Ta–Li(1)	2.69(2)	Li(1)–N(2)–Li(2)	99.6(7)
	2.99(2)		80.7(7)
Ta–Ba	3.5502(6)	Li(2)–N(2)–Li(2)	70.2(8)
	3.5406(7)	Ta–N(1)–Li(2)	100.6(6)
	3.4502(6)	Li(1)–N(1)–Li(2)	142.9(7)
Li(1)–Ba	2.971(8)	Ta–N(2)–Li(2)	146.6(6)
Li(2)–Ba	3.36(2)		142.8(6)
	3.27(2)	Li(1)–Ta–Li(1)	180.00(0)
	3.05(2)	Ta–Li(1)–Ta	180.00(0)
	2.93(2)	N(1)–Ba–N(1)	102.9(2)
Li(1)–Li(2)	2.90(2)		161.6(2)
Ba–Ba	4.055(1)	N(1)–Ba–N(2)	65.3(2)
	3.9672(8)		106.0(2)
	4.484(1)	N(1)–Ba–N(1)	70.4(2)
	3.9672(8)		78.0(2)
	3.9684(10)	N(1)–Ba–N(2)	74.7(2)
			140.5(2)
			84.1(2)
		N(2)–Ba–N(2)	94.0(2)
			123.9(2)

Each Ba atom has three nearest N(1) and three nearest N(2) neighbors whose distances range from 2.800(6) to 3.257(6) Å (Table 4), values comparable to those



• Ta ○ Ba ⊗ N(1) ● N(2) ⬭ Li(1) ▬ Li(2)

Fig. 2. A view perpendicular to the *bc* plane which shows (a) how Ta and Li(1) atoms are tetrahedrally coordinated and connected to each other and (b) how these Ta–Li(1) chains are linked together by Li(2) atoms in the *bc* plane.

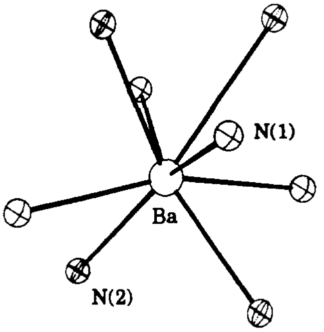


Fig. 3. A view of the Ba atom distorted dodecahedral coordination.

in Ba_2TaN_3 where distances vary from 2.771 to 3.462 Å. The eightfold Ba coordination is shown in Fig. 3. Two sets of two N(1) and two N(2) atoms describe trapezoids that comprise the arcs of a distorted dodecahedron.

It is interesting to compare the synthesis of $Li_3Ba_2TaN_4$ with that of Ba_2TaN_3. Both compounds resulted from the reaction of a mixture of Li, Ba and Ta metals with $N_2(g)$. A Li:Ba 2:1 molar ratio was used to prepare $Li_3Ba_2TaN_4$; a 1:1 molar ratio was used for the preparation of Ba_2TaN_3. The reaction temperature may be a more important factor than composition in determining which compound forms. $Li_3Ba_2TaN_4$ was prepared at 860 °C while Ba_2TaN_3 was prepared at 1000 °C. At the more elevated temperature Li_3N may escape from the Li–Ba–Ta–N system, favoring formation of Ba_2TaN_3.

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