

# Synthesis of the First Thorium-Containing Nitride Perovskite, TaThN<sub>3</sub>

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TaThN<sub>3</sub> can be prepared from a reaction of Ta<sub>2</sub>Th<sub>2</sub>O<sub>9</sub> and Ca<sub>3</sub>N<sub>2</sub> at 1100–1500°C or from a reaction of Ta<sub>3</sub>N<sub>5</sub> and Th<sub>3</sub>N<sub>4</sub> at 1400°C. This black polycrystalline material crystallizes in the perovskite structure type with  $a = 4.020(6)$  Å. © 1995 Academic Press, Inc.

## INTRODUCTION

Nitride and oxynitride perovskites are relatively uncommon, largely due to the high formal charges required of the cations. For a composition  $ABN_3$ , the oxidation state possibilities for  $A$  and  $B$  are (1, 8), (2, 7), (3, 6), and (4, 5). To date, only the (3, 6) combination has been explored (1); a (2, 5) combination is also known for oxynitrides such as BaTaO<sub>2</sub>N (2, 3).

The main difficulty arises in fully oxidizing the cations. The high charges required of the cations to counterbalance the 9- charge from the nitrogen atoms are generally unobserved in the binary nitrides. Tantalum is, in fact, the only early transition metal that readily forms a binary nitride in which the transition metal is in its highest possible oxidation state (4). While Ta<sub>3</sub>N<sub>5</sub> can be formed from TaCl<sub>5</sub> or Ta<sub>2</sub>O<sub>5</sub>, HfN and WN are the most nitrogen-rich bulk phases for its neighbors. Likewise, thorium is unique in its ability to form a binary nitride, in which it is formally in the 4+ valence state. To stabilize a ternary nitride, one would like to involve transition elements that are known to be readily oxidized by nitrogen (5). Therefore, both Ta and Th should be excellent components of ternary nitrides.

Materials like LaWN<sub>3-x</sub>O<sub>x</sub> have been studied for use as dielectrics (6, 7, 8), since the dielectric response varies with the O/N ratio and since the O/N ratio is easily adjustable over a wide range ( $x = 0.6 - 2.0$ ) (9). LaWN<sub>3-x</sub>O<sub>x</sub> is prepared from La<sub>2</sub>W<sub>2</sub>O<sub>9</sub> at 700°C under flowing NH<sub>3</sub>. The nonintegral oxidation state of W suggests a means for their observed electrical properties.

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The structure of LaWN<sub>3-x</sub>O<sub>x</sub> has been determined by neutron diffraction (1) and found to be best described in the noncentrosymmetric spacegroup  $I\bar{4}$ . It is known that noncentrosymmetric transition metal compounds with delocalized excited states and a moderate to large bandgap should have nonlinear optical responses, namely large second harmonic generation. Wiegel *et al.* have noted the responses in pure oxide niobates and titanates (10). It seems reasonable to expect a strong NLO response in nitride perovskites, since they show a propensity toward noncentrosymmetry and since their more-covalent  $M-N$  bonds should yield smaller bandgaps than their oxide counterparts. However, TaTh(N,O)<sub>3</sub> and LaW(N,O)<sub>3</sub> are black, probably due to the disorder in their anionic networks. Pure nitride phases are extremely difficult to prepare, so the search for useful NLO materials in the oxynitride perovskite system must continue.

## SYNTHESIS

Th<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> can be prepared from the binary oxides at 1380°C (11). These reactions were carried out in welded Ta ampoules to reduce the possibility of Th release to the laboratory. Th<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> does not react with flowing NH<sub>3</sub> up to 1000°C. Reactions of Th<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> with Ca<sub>3</sub>N<sub>2</sub>, however, produced CaO and the black, air-sensitive perovskite phase, TaTh(O,N)<sub>3</sub>. There was always a trace of TaN<sub>x</sub>, a product of a reaction with the Ta tube wall, as Ca<sub>3</sub>N<sub>2</sub> certainly decomposes before the ternary-forming reaction takes place. The presence of impurities precluded any bulk N analysis. These reactions were carried out at higher temperatures ( $T = 1100-1500^\circ\text{C}$ ). Similar treatments of Th<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> (12) did not yield perovskite phases.

Ta<sub>3</sub>N<sub>5</sub> was prepared from TaCl<sub>5</sub> in flowing ammonia, as described previously (4, 13); little or no Cl is present in the final product, as determined by EDAX analysis. Th<sub>3</sub>N<sub>4</sub> can be prepared from the combination of the elements at 700–1300°C (14); however, we produced Th<sub>3</sub>N<sub>4</sub> from a reaction of ThCl<sub>4</sub> with LiNH<sub>2</sub> in liquid ammonia. The Th(NH<sub>2</sub>)<sub>4</sub> ·  $n$ NH<sub>3</sub>/LiCl mixture was washed several times with liquid ammonia. The resultant amorphous material

TABLE 1  
X-Ray Diffraction Intensity Comparison of Some TaThN<sub>3</sub>  
Structural Models versus the Observed Intensities

<i>h</i>	<i>k</i>	<i>l</i>	2θ	<i>d</i>	<i>I</i> (CsCl)	<i>I</i> (perov.)	<i>I</i> (TaThN <sub>2.5</sub> )	<i>I</i> (obs)
1	0	0	22.09	4.020	18.7	10	11.3	
1	1	0	31.45	2.843	1000	1000	1000	1000
1	1	1	38.77	2.321	6.4	21.6	18.2	[155]
2	0	0	45.07	2.010	189.3	245.9	235.4	348
2	1	0	50.74	1.798	9.5	6.7	7.1	
2	1	1	55.99	1.641	402.3	410.3	408.9	[764]
2	2	0	65.64	1.421	125.6	157.7	151.9	177
3	0	0	70.18	1.340	1.1	0.8	0.9	
2	2	1	70.18	1.340	4.3	3.4	3.5	
3	1	0	74.59	1.271	175.2	180.2	179.3	320
3	1	1	78.92	1.212	3.5	7.8	6.9	

Note. The nitrogen content makes very little contribution to the diffraction intensities. Observed intensities in square brackets include the intensity of overlapping Th<sub>2</sub>N<sub>2</sub>O peaks.

was heated to 900°C under purified, flowing N<sub>2</sub> to yield crystalline Th<sub>3</sub>N<sub>4</sub> and a trace of Th<sub>2</sub>N<sub>2</sub>O (1–5 mole%). Excess LiCl condensed at the cold end of the tube.

Reaction of the binary nitrides, Ta<sub>3</sub>N<sub>5</sub> and Th<sub>3</sub>N<sub>4</sub>, at 1400°C results in an air-sensitive perovskite phase. Again the product was always contaminated with a small amount of TaN<sub>x</sub> and, in this case, some Th<sub>2</sub>N<sub>2</sub>O (1–5 mole%, as estimated from X-ray diffraction data).

## RESULTS AND DISCUSSION

X-ray diffraction patterns were collected on a Scintag XDS2000 θ–θ diffractometer, fitted with a solid-state detector. The sample was protected from the atmosphere by a mylar film during the data collection. The peaks from an automatic peak-finding routine using the Pearson VII function were indexed on a primitive cubic cell, *a* = 4.020(6) Å. Materials made from oxide precursors as well as those produced from the binary nitrides had the same lattice parameters within the estimated standard deviation.

The metal atoms in the perovskite structure are located in the same positions as in the CsCl structure. In fact, the material La<sub>2</sub>U<sub>2</sub>N<sub>5</sub> has been observed by Waldhart and Etmayer (15) with a structure related to perovskite (or CsCl) but with a tetragonal distortion to accommodate a deficit of nitrogen atoms. LAZY-PULVERIX (16) calculations for an ideal perovskite, “Ta<sub>2</sub>Th<sub>2</sub>N<sub>5</sub>” (modeled after La<sub>2</sub>U<sub>2</sub>N<sub>5</sub>), and “ThTa” (modeled after CsCl) are given in Table 1. The X-ray diffraction data is not sufficiently sensitive to nitrogen to discern between these models. Nevertheless, no splitting was observed which would support the tetragonal model. Furthermore, the pure intermetallic possibility can be eliminated, since the material gives off an ammonia odor when exposed to water, indicating the

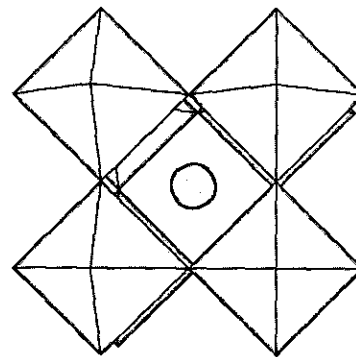


FIG. 1. The ideal perovskite structure. Ta atoms center the N<sub>6</sub> octahedra. Large circles represent Th atoms. N atoms are located at the vertices of the octahedra.

presence of an ionic nitride. Therefore, we favor the full perovskite model which is depicted in Fig. 1. We cannot, however, preclude a small partial substitution of oxygen for nitrogen in the material.

One expects bond valences of 5/6 for the Ta–N bonds and bonds of valence 4/12 for the Th–N bonds, since Ta and Th are in 6- and 12-coordination, respectively (for a review, see (17, 18)). Using the available nitride bond valence parameters (5), one expects *d*(Th–N) = 2.75 Å (obs. 2.84 Å) and *d*(Ta–N) = 2.07 Å (obs. 2.01 Å). The longer than expected *d*(Th–N) and the shorter than expected *d*(Ta–N) indicate some competition between those two attractive forces which could easily give rise to a distortion from cubic symmetry. Any distortion from cubic symmetry would probably be due primarily to the anions; this effect is not observable from X-ray powder diffraction data.

Madelung potentials, calculated using the Ewald method (19), and bond valence sums are listed in Table 2. We have shown previously that the site potentials in nitrides are roughly  $-12q$  volts, where *q* is the formal oxidation state (5). The site potential for Th seems low, but this is expected, since the Th–N bonds are the longer ones. Note that the potentials scale as 1/*d*. Similar site potentials are seen in Th<sub>3</sub>N<sub>4</sub> (14) and the Th<sub>2</sub>N<sub>2</sub>Q (Q = O, S, Se, Te) (20–22) series (5).

Finally, it is irresistible to comment on the parallels between TaThN<sub>3</sub> and the oxide superconductors. Histori-

TABLE 2  
Bond Valence Sums and Madelung Potentials for TaThN<sub>3</sub>  
(*a* = 4.020 Å) with the Ideal Perovskite Structure

Atom	Bond valence sum	Charge ( <i>q</i> )	Potential ( <i>V</i> )
Ta	5.84	5.00	–59.22
Th	3.09	4.00	–36.24
N	2.98	–3.00	32.95

cally, nitrides have shown considerable promise as superconductors with critical temperatures predicted up to about 30 K (23–26). The boom in superconductivity research in the last 10 years spilled back into the nitride arena (27). With the same perovskite building blocks being present in both oxide superconductor and ternary nitride systems, one can again envision nitride chemistry playing a role in superconductivity research. Successes in novel, layered nitride systems are emerging (28).

We have prepared the first Th-containing nitride perovskite. It crystallizes in the spacegroup  $Pm\bar{3}m$  with  $a = 4.020(6)$  Å. We have described the use of metathesis reactions to form ternary nitrides from ternary oxides; this technique is general and should yield a plethora of new materials. The propensity of nitrides for noncentrosymmetry and their covalent bonds render the nitride system a potential hunting ground for NLO materials.

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