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Microwave Synthesis of Ternary Nitride Materials

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The utility of microwave heating and microwave generated nitrogen plasmas as a synthetic technique toward the synthesis of nitrides is demonstrated. The synthesis of several binary and ternary nitrides, including TiN, AlN, VN, Li_3FeN_2, Li_5TiN_3, and Li_3AlN_2, using either a microwave heating source or a microwave generated nitrogen plasma, are described. Two types of reactions, those between a metal and a nitrogen plasma and those between Li_3N and either a metal or a metal nitride in a microwave heating system are discussed.

INTRODUCTION

Solid-state reactions are often plagued by extremely long reaction times caused by slow diffusion rates in solids. Consequently, the use of alternative synthesis techniques (solid state precursors, molecular precursors, fluxes, etc.) have been explored in order to achieve faster reaction rates. Interest has also been shown in alternative heating techniques, for example induction heating, arc furnaces, and microwave heating. Several research groups have recently demonstrated the utility of microwaves as a heating source in the synthesis of a number of solid-state materials, such as chalcopyrite semiconductors (1), metal dichalcogenides (2), oxide superconductors (3), and metal halides (4). All these microwave techniques take advantage of the rapid resistive heating of fine metal particles caused by electrical currents induced in them by the microwave field. Using relatively low-power microwave generators, such as those found in standard home-use microwave ovens, many metal powders will heat rapidly and without noticeable electrical discharges. Such heating techniques have been extended to include the synthesis of binary nitrides such as TiN (2), Cr_2N (2), and AlN (5) by heating the metal powder under nitrogen gas in a microwave, where the use of the microwave heating source can lower the synthesis time from days to hours or minutes.

Traditional synthetic routes to nitrides usually require high temperatures and long synthesis times that can make the synthesis experimentally tedious. For ternary and higher nitrides, microwave heating offers several advantages over conventional heating methods, including greatly shortened reaction times. In addition, since microwaves heat the reactant particles uniformly, thermal losses from the surfaces of the particles set up thermal gradients which are inverse to those found in conventionally heated samples. These gradients could help overcome the strong diffusion barriers set up by the formation of nitride coatings on the surface of the reactant particles. In addition, some evidence exists for enhanced diffusion rates in solid materials that are exposed to microwave radiation (6, 7). Finally, by using microwaves, the rate of heating and subsequent cooling are both extremely rapid (up to 100°C/sec). Such high heating and cooling rates could potentially lead to kinetic phases that could not be easily obtained by other routes, but will certainly lead to shorter overall reaction times due to shorter ramp times to and from the reaction temperature. In this paper, we report the synthesis of several binary and ternary nitride materials using two microwave heating sources.

EXPERIMENTAL

Synthesis of MN_x ($M = Ti, Al, V, Si, B, Nb$)

The synthesis of metal nitrides using microwaves as the heating source was carried out by placing approximately 2 grams of the metal powder (Ti: Alfa, 99.4%, −100 mesh; Al: Cerac, 99.97%, +325 mesh; Si: Aesar, 99.5%, −325 mesh; V: Alfa, 99.5%, −325 mesh; B: Cerac, 99.5%, −100 mesh; Nb: Cerac, 99.8%, −100 + 325 mesh) contained in an alumina sample holder into a microwave cavity (Sanyo model EM-604TW, 600W, 2.450 GHz, Fig. 1) under nitrogen at atmospheric pressure. The metal powder was exposed to microwave radiation for 20 minutes, ground, and reheated for an additional 20 minutes.

Alternatively, the powdered metal sample was placed in a plasma applicator attached to a low ripple microwave source (Cober Electronics model 9338/S1.2M, 1200 W, 2.45 GHz, Fig. 2). The apparatus was evacuated and purged with nitrogen. A final nitrogen pressure of ∼5 Torr was

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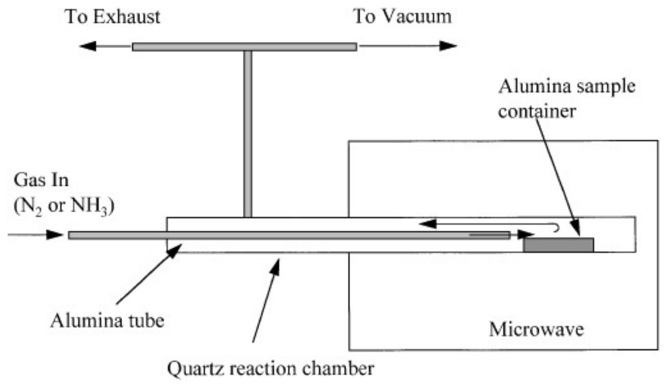

FIG. 1. Schematic diagram of Sanyo microwave system used in the synthesis of nitride materials.

used to maintain a steady plasma. The sample was then heated under a nitrogen plasma for 3 h, ground, and reheated under a nitrogen plasma for an additional 3 h. For samples which did not readily ignite the plasma, Ti powder in an adjacent alumina boat was used to spark the plasma. Once the plasma was sparked, it could be sustained by the microwave field and the boat containing the reactant was moved into it. Powder X-ray diffraction analysis of all products was performed on a Siemens D5000 diffractometer at 40 kV and 45 mA with Cu$K\alpha$ radiation.

Synthesis of $Li_{2x-3}M^{+x}N_{x-1}$ from Li_3M and a Metal ($M = Fe, Al, Si, Ti$)

The synthesis of ternary nitrides containing lithium ($Li_{2x-3}M^{+x}N_{x-1}$) was carried out by grinding together the metal powder (Fe(Aldrich, 99.9 + %), Al(Cerac, 99.97%, +325), Si(Aesar, 99.5%, −325 mesh), Ti(Alfa/Aesar, 99.4%, −100 mesh)) with a slight molar excess of Li_3N (Cerac, 99.5%, −60 mesh) in an argon-filled glove box. The reaction mixture was placed in an alumina boat, which was then placed inside a quartz reaction chamber. The reaction chamber was inserted into the microwave cavity along with a beaker of water which was used as a dummy load to protect the magnetron from reflected power. Figure 1 shows a schematic diagram of the sample holder for use in the microwave cavity. The chamber was purged with N_2 before heating the reaction mixture in one-minute cycles through microwave irradiation. After 8–10 one-minute cycles, additional Li_3N was added to the sample and the mixture was reheated in the microwave under N_2 for 8–10 one-minute cycles.

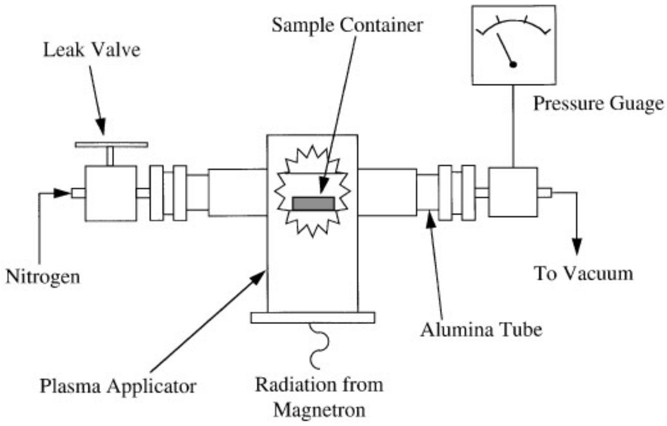

FIG. 2. Schematic diagram of Cober microwave system used in the synthesis of binary nitride materials by reaction with a nitrogen plasma.

Sealed Tube Synthesis of $Li_{2x-3}M^{+x}N_{x-1}$ from Li_3N and Metal Nitride ($M = Al, Ta, B$)

$Li_{2x-3}M^{+x}N_{x-1}$ *was synthesized by grinding together the metal nitride* (AlN: Cerac, 99.5%; Ta_3N_5: synthesized by reacting Ta_2O_5 with ammonia under flow through conditions for 2 days at 900°C; BN: Alfa, 99.5%) with a slight molar excess of Li_3N (Cerac, 99.5%, −60 mesh) to yield a total sample mass of approximately 1.5 grams. The mixture was placed inside a quartz tube which was closed on one end and connected to a valve via an Ultra-Torr connector on the other end. The sample container was evacuated slightly and placed in the microwave. A beaker of water was used as a dummy load to protect the magnetron head from reflected energy. The sample was heated in 10-minute cycles until a reaction was started (typically 20 minutes total time). Microwave power was applied for an additional 10 minutes after visible signs of the reaction had ceased to ensure completion.

RESULTS AND DISCUSSION

Two general reaction schemes were used to prepare the nitrides discussed in this paper and listed in Table 1. For those ternary materials for which nitride reactants of sufficiently high nitrogen content were available, syntheses could be carried out as

$$Li_3N + AlN \rightarrow Li_3AlN_2. \qquad [1]$$

The reactants were placed into a quartz tube, evacuated, and exposed to microwave radiation. Alternatively, for the synthesis of materials for which nitrogen uptake is required, for example the reactions listed in Eqs. [2] and [3], the reactants can be heated under a nitrogen plasma.

$$M \xrightarrow{\mathrm{N(plasma)}} M\mathrm{N} \qquad [2]$$

$$Li_3N + M \xrightarrow{\mathrm{N(plasma)}} Li_{2x-3}M^{+x}N_{x-1}. \qquad [3]$$

In the following sections, both reaction pathways will be discussed.

TABLE 1

Reactants	Conditions	Products
Ti	N_2 with grinding	TiN
B	N_2 with grinding	BN + B
Al	N_2	AlN
Si	N_2 with grinding	α,β-Si_3N_4 + Si
V	N_2 with grinding	VN
Nb	N_2 with grinding	NbN, Nb_2N, Nb_3N_4
Li_3N + Al	N_2 + additional Li_3N	Li_3AlN_2 + AlN
Li_3N + AlN	Vacuum	Li_3AlN_2
Li_3N(*xs*) + BN	Vacuum	Li_3BN_2 + Li_3N
Li_3N + Fe	N_2	Li_3FeN_2 + Fe
Li_3N + Si	N_2	$LiSi_2N_3$ + Si
Li_3N + Si_3N_4	Vacuum	Li_2SiN_2 + Li_5SiN_3 + $Li_{18}Si_3N_{10}$
Li_3N + Ti	N_2	Li_5TiN_3 + Ti + TiN
Li_3N + Ta_3N_5	Quartz tube under vacuum	Li_7TaN_4 + Li_3N + TaN
Li_3N + Ta_3N_5	Vacuum	New lithium tantalum nitride phase

Synthesis of Binary Nitrides

Preliminary experiments to determine the viability of microwaves for the bulk synthesis of binary nitride powders consisted of the reaction of a metal powder with nitrogen. While several metal powders were found to heat well in a conventional home-use microwave, most did not demonstrate appreciable nitride formation. The most notable exception was titanium powder, over which a nitrogen plasma was readily sparked, resulting in the formation of a TiN coating on the titanium particles.

After ~20 minutes of microwave heating, the color of the titanium powder had changed to the characteristic gold color of TiN, confirming the report by Whittaker and Mingos (2). However, powder X-ray diffraction analysis of the product revealed the presence of unreacted titanium metal in the product. Incomplete reaction has been observed in other microwave reactions between a metal powder and N_2. For example, in the formation of AlN from Al under N_2, residual Al is seen in the product as well as an Al_2O_3 impurity, presumably from water or oxygen in the gas stream (5). The incomplete conversion of aluminum powder to aluminum nitride was attributed to the formation of a layer of aluminum nitride on the surface of the metal particles, which slows nitrogen diffusion into the interior of the particles (5). This is consistent with our observation of unreacted Ti and with the notoriously slow diffusion of nitrogen through TiN.

The formation of a nitrogen plasma over the reactant metal powder was found to greatly enhance the rate of nitride formation. However, in a domestic microwave, it was not possible to sustain a plasma discharge over the titanium sample and the nonuniform nature of the microwave field led to uneven heating. In addition, the titanium samples heat rapidly to glowing yellow heat after which no plasma discharges are observed. Therefore, the synthesis of TiN was attempted in a plasma applicator attached to a 1.2 kW low-ripple microwave source. In this instrument, it was possible to generate and sustain a nitrogen plasma under reduced nitrogen pressure (~5 Torr). Heating titanium metal in this nitrogen plasma for 3 hours leads to a powder with a golden color, indicative of TiN. However, powder X-ray diffraction analysis reveals the product to be a mixture of TiN and Ti_2N. Grinding the sample briefly and heating it for an additional 3 hours results in complete conversion to TiN as evidenced by powder X-ray diffraction (Fig. 3).

Elemental powders over which a plasma did not ignite (B, Si) did not form a nitride product. However, a plasma could be ignited for these compounds by placing a small amount of titanium powder in one end of the reaction vessel or in an adjacent alumina boat. Nitrogen plasmas are readily sparked over titanium powder and, in the plasma applicator, once formed are easily sustained. The reaction vessel is then positioned to place the desired reactant within the plasma. Table 1 lists several binary nitrides which were synthesized by reaction of the metal powder with a nitrogen plasma. AlN is readily formed in the nitrogen plasma (Fig. 4), even without an intermediate grinding step with a total reaction time of ~3 hours. VN required one intermediate grinding after about 3 hours of treatment with the nitrogen plasma, followed by another 3-hour microwave treatment (Fig. 5). Reactions with Nb, Si, and B were less successful, yielding incomplete reactions and multiphasic products even after repeated intermediate grindings. The reaction of niobium metal with a nitrogen plasma yields a mixture of NbN, Nb_2N, and Nb_3N_4 as well as NbO_2 formed from residual oxygen in the nitrogen feed gas. Reaction of the nitrogen plasma with silicon yields small amounts of both

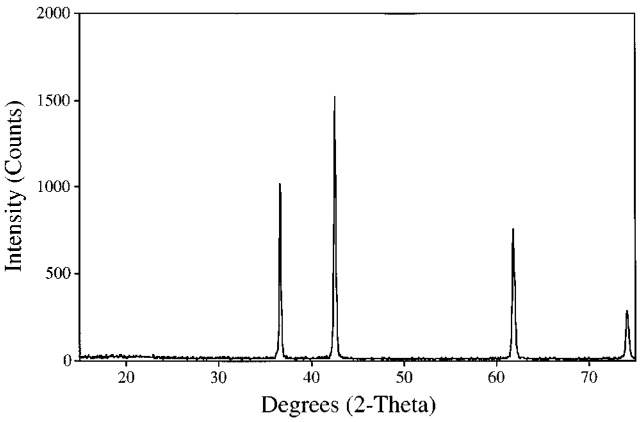

FIG. 3. Powder X-ray diffraction pattern of TiN synthesized from the reaction of Ti powder with N_2 gas in a plasma applicator.

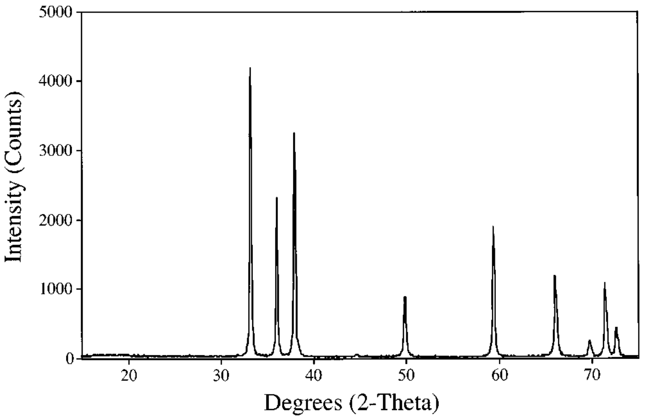

FIG. 4. Powder X-ray diffraction pattern of AlN synthesized from the reaction of Al powder with N_2 gas in a plasma applicator.

α and β-Si_3N_4, with the predominant phase being unreacted Si. The reaction of the plasma with boron is also incomplete and even after several intermediate grindings, only half of the boron powder can be converted into poorly crystalline turbostractic BN.

Despite the presence of small amounts of oxide impurities present in several products, the total amount of these impurity phases is very small. In the case of titanium, trace amounts of TiO can be removed by treatment with a 95% nitrogen/5% hydrogen plasma, which appears to scavenge oxygen from the substrate. Indeed, as we reported elsewhere (8), the oxides of several transition and main group metals can be completely converted to the respective nitride products by treatment with a nitrogen/hydrogen plasma, even if the corresponding ammolnolysis reactions are thermodynamically unfavorable. The presence of small amounts of hydrogen in a nitriding plasma has been demonstrated to yield enhanced nitridation rates (9) in addition to its ability to remove oxygen impurities.

Synthesis of Ternary Nitrides

Lithium and lithium nitride are attractive starting materials for the synthesis of ternary nitrides for a number of reasons. Lithium is an electronic conductor and lithium nitride is an ionic conductor and, as such, both heat well when exposed to microwave radiation. Both materials melt at moderate temperatures and can be used as reactive fluxes. Many ternary nitrides containing lithium are known, greatly simplifying the task of product characterization. Finally, there has been some interest in lithium containing nitride for use as lithium solid electrolytes (10, 11) and as cathode materials (12) for lithium ion batteries.

Attempts were made to synthesize several lithium containing ternary nitride materials starting from lithium nitride and the metal as shown in Eq. [3]. Early experiments revealed that the extremely rapid heating of the metal particles can lead to evaporation of Li_3N from the reaction mixture and incomplete product formation. For example, the reaction of iron powder with Li_3N leads to the formation of Li_3FeN_2 and Fe (Fig. 6) due to the loss of Li from the reaction. The rate of lithium evaporation was slowed by observing several precautions. For example, if the reaction is stopped when the sample mixture begins to glow yellow-hot, the time that the reaction mixture spends at very high temperatures is limited and the evaporation of Li and Li_3N is slowed. Once all the lithium has either evaporated or reacted, the reaction can be driven closer to completion by the addition of more lithium followed by an additional one minute heating cycle. For example, the reaction of Li_3N and Al with N_2 leads to the formation of Li_3AlN_2 and AlN in $\sim$1 : 2 ratio as evidenced by powder X-ray diffraction. Addition of lithium metal to this mixture results in a

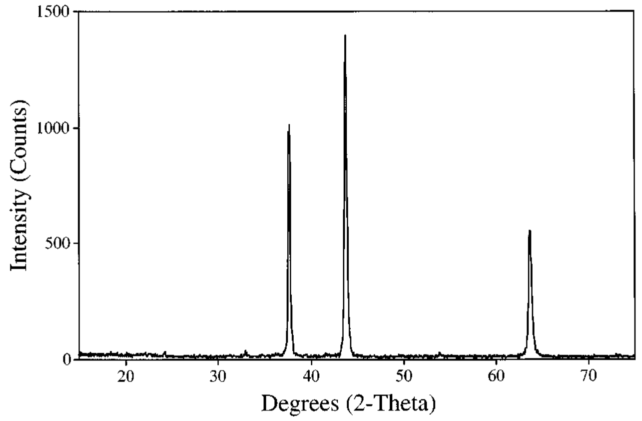

FIG. 5. Powder X-ray diffraction pattern of VN synthesized from the reaction of V powder with N_2 gas in a plasma applicator.

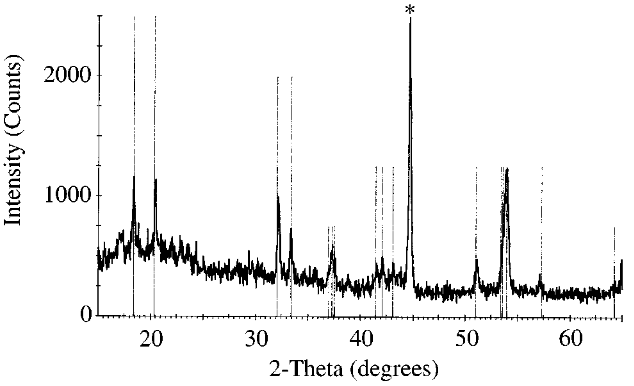

FIG. 6. Powder X-ray diffraction pattern of Li_3FeN_2 synthesized from the reaction of Fe powder and Li_3N under N_2 gas in the microwave. (*) indicates Fe. Lines indicate peak positions of Li_3FeN_2 (JCPDS = 20–626).

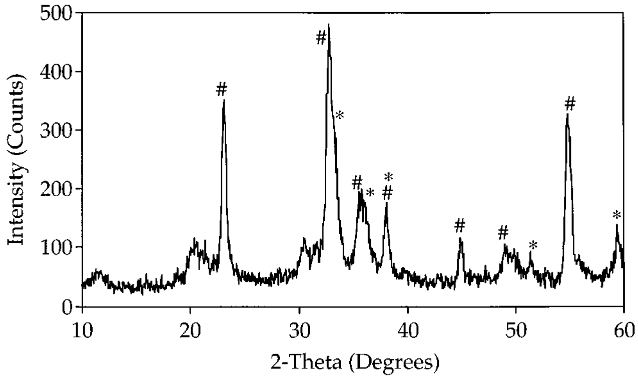

FIG. 7. Powder X-ray diffraction pattern of Li_3AlN_2 synthesized from the reaction of Al powder and Li_3N under N_2 gas in the microwave. (*) indicates AlN; (#) indicates Li_3AlN_2.

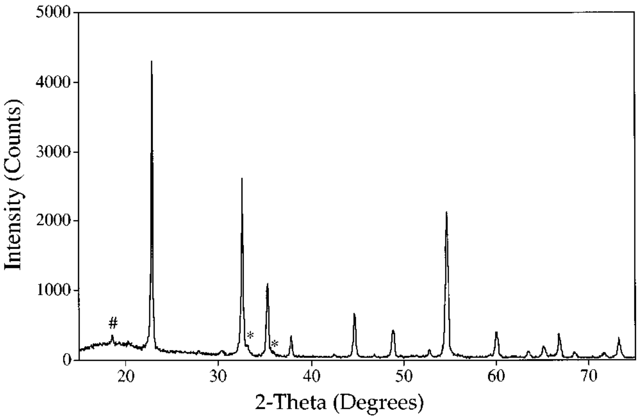

FIG. 8. Powder X-ray diffraction pattern of Li_3AlN_2 synthesized from the reaction of AlN and Li_3N in a microwave. (*) indicates AlN; (#) indicates $LiAlO_2$.

Li_3AlN_2 : AlN ratio of ~3 : 1 after additional heating cycles (Fig. 7). In Table 1, several other reactions between Li_3N and a metal, which also yield incomplete reactions, are shown.

The reaction between Li_3N and a metal did not yield clean products, even after three successive additions of Li_3N to account for the lithium lost during heating. To restrict the loss of lithium nitride further, the amount of free volume in the reaction vessel was limited, yielding less space to which the lithium could diffuse. Also, the final reaction temperature and thermal runaway was limited by using two nitride reactants, one of which is an electrical insulator. The theoretical reaction is

$$(2x-3)\mathrm{Li_3N} + M^{+x}\mathrm{N}_{x/3} \rightarrow \mathrm{Li}_{2x-3}M^{+x}\mathrm{N}_{2x-1}. \quad [4]$$

However, such a reaction pathway limits the final nitrogen content to the amount of nitrogen present in the reactants. In order to synthesize high nitrogen content products using lithium nitride as a starting material, transition or main group metal nitrides with a metal to nitrogen ratio of at least 1 : 1 must be used, eliminating most if not all of the late transition metals.

Starting with two nitride reactants resulted in a greatly improved yield and product crystallinity. The reaction of a 1 : 1 molar mixture of Li_3N and AlN heats only slowly initially and the sample must be exposed to 15–20 minutes of radiation before the onset of thermal runaway, after which the reaction mixture melts. Such behavior has been observed in other solid-state materials (13). The reaction of Li_3N and AlN is quite rapid, proceeding to completion in a couple of minutes after onset of thermal runaway. The sample was heated for several minutes after all visible signs of the reaction had subsided to assure complete reaction. After a total heating time of 40 minutes, a small amount of AlN was still present as demonstrated by powder X-ray diffraction. The amount of AlN can be virtually eliminated by the addition of more Li_3N and further heat treatment as shown in Fig. 8. Several small impurity peaks are observed: $LiAlO_2$, resulting from reaction with the walls of the quartz vessel, and a very small amount of AlN, residual starting material.

Other ternary nitride materials can be made using lithium nitride and the group XIII nitrides. For example, heating a 2 : 1 molar ratio of Li_3N and BN in the plasma applicator results in the formation of Li_3BN_2 and residual Li_3N. Excess Li_3N is needed in order for the sample to heat, since BN does not heat when exposed to a microwave field. Furthermore, microwave heating is a volumetric effect and the presence of a material in the reactant mixture which does not heat well significantly limits the ability of the sample to heat. The low density of BN further exacerbates the volumetric heating problem over other systems which include an electrically insulating reactant, most notably Li_3N and AlN.

The reaction of a 5.1 : 1 molar mixture of Li_3N and Si_3N_4 leads to the formation of a mixture of products (Li_2SiN_2, Li_5SiN_3, and $Li_{18}Si_3N_{10}$) due to the lack of thermal control in our microwave setup. A large number of lithium silicon nitrides are known with lithium : silicon ratios ranging between 2 : 1 and 8 : 1, all of which are readily interconvertable. Without the ability to maintain the sample temperature slightly below the melting point of lithium nitride, lithium nitride is lost from the reaction mixture, resulting in a mixture of several phases.

When a 7 : 1 molar mixture of Li_3N and Ta_3N_5 is heated in a microwave cavity under vacuum for less than 20 minutes, the cubic phase Li_7TaN_4 (14) can be obtained. Again the reaction is slow to initiate, but proceeds rapidly once thermal runaway begins. The product is black polycrystalline Li_7TaN_4 along with residual Li_3N and TaN. If the

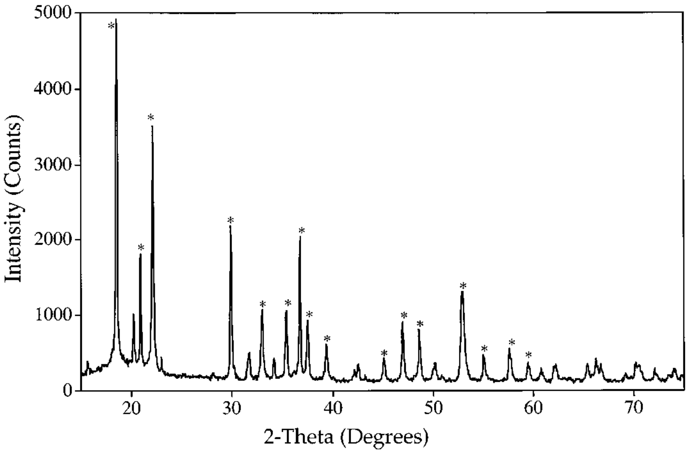

FIG. 9. Powder X-ray diffraction pattern of the new orthorhombic lithium tantalum nitride phase (peaks marked by (*), $a = 5.171(1)$, $b = 8.462(2)$, $c = 12.765(3)$). Other peaks correspond to Li_7TaN_4.

reaction is allowed to proceed for longer than 20 minutes, a previously unknown phase is obtained. This unknown phase (Fig. 9) can be indexed as orthorhombic ($\mathbf{a} = 5.171(1)$ Å, $\mathbf{b} = 8.462(2)$ Å, $\mathbf{c} = 12.765(3)$ Å). Further characterization will be reported elsewhere.

CONCLUSION

The utility of microwave heating and microwave generated plasmas as synthetic techniques toward the synthesis of nitride materials has been demonstrated. The reaction of several metal powders with a nitrogen plasma has been shown to yield binary nitrides with total reaction times under 6 hours. In addition, the reaction of Li_3N was either a metal or a metal nitride has been demonstrated to yield ternary nitride phases in impressively short reaction times. With careful selection of starting materials, the number of materials which can potentially be synthesized is quite large.

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