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Solvothermal Synthesis of Nanocrystalline Copper Nitride from an Energetically Unstable Copper Azide Precursor

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Nonaqueous solvothermal chemical reactions have found extensive utility in the growth of inorganic non-oxide materials. This report describes the successful use of organic solvothermal environments to synthesize energetically unstable copper azide precursors that are then decomposed in situ to crystalline metastable copper nitride at temperatures below 200 °C. A comparison of Cu_3N products formed from nonpolar (toluene) and coordinating (THF) solvents is described. The cubic Cu_3N products are nanocrystalline with aggregated particle-like extended structures and were characterized by X-ray diffraction, electron microscopy, IR spectroscopy, and mass spectrometry. The thermal stability and composition of Cu_3N was examined by thermogravimetric analysis and bulk elemental analysis. The particle surfaces contain bound residual solvent species that can be removed by heating. The poorly coordinating solvent, toluene, lead to a more crystalline product containing less residual organic content. Benchtop reactions were performed to follow the temporal formation and decomposition of metal azide intermediates. These studies provided more detailed information on the progression of metal azide to metal nitride materials in a solvothermal environment.

Introduction and Background

Many simple transition-metal nitrides (MN_x) have been extensively studied over the past 50 years.[1] In most cases, these studies have focused on the thermodynamically stable nitrides obtained from Group 3−6 metals. For example, Group 4 and 5 nitrides such as TiN, ZrN, and NbN are refractory materials with high melting points ($\geq$2200 °C) and most are conventionally produced by high-temperature reactions (~1000 °C) between elemental metals, metal oxides, or halides and N_2 or NH_3. In recent years, there are notable synthetic routes to films and powders of the early to mid transition-metal nitrides that utilize molecular or polymeric precursor decomposition reactions, usually along with NH_3, that occur at moderate temperatures (~500 °C).[2]

Upon examination of the nitride literature, it is apparent that there are few viable synthetic routes reported for the less thermally stable mid to late transition-metal nitrides. For example, the late transition metals (e.g., Fe, Ni, and Cu) uptake nitrogen to a small extent and often form metal-rich nitrides, such as M_3N and M_4N. Many of these nitrides evolve N_2 gas upon modest heating below 800 °C and decompose to metallic elements; thus, they are difficult to synthesize by conventional high-temperature synthetic methods. The metal-rich nitrides have physical and chemical properties that manifest themselves in a variety of ways, including correlated magnetic interactions, small band gap semiconductor behavior, and reactive catalytic surface structures. Some low-oxidation state, metal-rich structures are also amenable to reductive lithiation or intercalation reactions forming compounds such as Li_xM_3N (M = Cu, Ni, Co) that have potential as battery electrode materials.[3] Perhaps as a result of their thermodynamic instability, late transition-metal nitrides are most often studied as a compo-

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nent in more themodynamically stable ternary systems $M_xM'_yN_z$ that are synthesized at relatively high temperatures (e.g., $FeWN_2$,[4] Ni_2Mo_3N,[5] and $Ni_{2-x}Co_xMo_3N$[6]). Several recent reviews show that the ternary nitrides exhibit extensive structural and compositional variety.[7]

Successful syntheses of the metal-rich and often thermally sensitive mid to late transition-metal nitrides (M_xN, $x > 1$) are generally accomplished using metal ammonia or metal amine precursors, such as salts containing $M(NH_3)_x$ or $M(NH_2)_y$ species. These precursors are converted to crystalline metal nitrides via elevated temperature reactions with gaseous or supercritical ammonia. The nitrides prepared by these methods include Co_3N,[8] Ni_3N,[8,9] and Cu_3N.[8,10] Thin films of several of these metal-rich nitrides, most commonly Cu_3N, have also been produced by metal or metal precursor reactions with nitrogen plasmas or ammonia.[11] The thermal instability of semiconducting Cu_3N films was utilized to selectively deposit copper islands for use in optical recording media.[12]

Over the past decade, rapid and exothermic solid-state metathesis (SSM) reactions have been utilized to synthesize crystalline early transition-metal nitrides from metal halides and reactive solid nitrogen sources (e.g., Li_3N, Mg_3N_2, and NaN_3).[13] Since SSM reactions can reach very high transient temperatures (~1300 °C), they usually produce thermodynamically stable metal nitrides. Exothermic SSM syntheses of thermally sensitive late transition-metal nitrides, such as Cu_3N and Ni_3N, not surprisingly, produce elemental metals because the transient reaction temperatures exceed the thermal decomposition point of the product nitride.[13b]

One way to moderate temperatures in exothermic metathesis reactions is to use a nonaqueous solvent environment; for example, organic solvents are frequently used at low temperatures (<0 °C) in organomagnesium Grignard or alkyllithium reactions with metal halides. High-temperature (~300 °C) solvothermal methods are extensively utilized in the synthesis of well-defined nanoparticles and nanocrystals.[14] It is reasonable to expect that if SSM-based metal nitride reactions proceed in a slower, moderate-temperature solvothermal context, they may be viable routes to thermally unstable (metastable) metal nitrides. There is some precedence for metal nitride formation using solvothermal reactions with Li_3N and NaN_3; for example, nanocrystalline TiN powder is produced by the reaction of $TiCl_4$ and NaN_3 in superheated benzene at 380 °C,[15] nanocrystalline GaN is produced from $GaCl_3$ and Li_3N in benzene at 280 °C,[16] and amorphous/poorly crystalline GaN forms from $GaCl_3$ and NaN_3 in toluene at 260 °C.[17]

In the current study, we describe the successful utilization of solvent-moderated metathesis reactions that combine the formation of an energetically unstable metal azide precursor with in situ metal azide decomposition to produce crystalline metastable copper nitride, Cu_3N, from $CuCl_2$ and NaN_3 in superheated solvents (toluene and THF) below 200 °C. The copper nitride products are nanocrystalline, have nanometer and micrometer-sized particle and aggregate morphologies, show moderate thermal sensitivity, and decompose to elemental copper on heating under inert conditions near 400 °C. A variable temperature solvothermal reaction study on Cu_3N formation provides direct evidence that copper azide intermediates and reduced copper azide and chloride species are produced during this solvothermal metathesis reaction. This synthetic approach should be applicable to the growth of other nanocrystalline metastable metal nitrides.

Experimental Section

Solvothermal Synthetic Methods. Toluene ($C_6H_5CH_3$, Fisher Scientific, certified) and tetrahydrofuran (THF, C_4H_8O Fisher Scientific, certified) were dried over sodium or potassium and distilled prior to use, while *m*-xylene (*m*-dimethylbenzene, $C_6H_5(CH_3)_2$, Aldrich 99% anhydrous H_2O < 0.01%) was used as received. A typical Cu_3N synthesis in toluene utilized the following anhydrous reagents (used as received): $CuCl_2$ (3.74 g, 27.8 mmol, Alfa Aesar, 99%) and NaN_3 (3.63 g, 55.8 mmol, Aldrich, 99%)]. Note that the molar ratio of metal chloride to NaN_3 used is 1:2 to ensure that all chloride is sequestered as NaCl. Equivalent reactions performed in THF were run at half the scale of toluene reactions for safety reasons described in the text.

A high-temperature, high-pressure stainless steel reactor (125 mL, Parr Instruments Model 4752, 3000 psi maximum pressure) was loaded in an argon-filled glovebox (Vacuum Atmospheres MO-40M) with anhydrous copper chloride powder and a stoichiometric amount of sodium azide. The solid reagents were separately ground with a mortar and pestle and used as fine powders. The reactor containing the powder mixture and a Teflon-coated stir bar was partially filled with degassed toluene or THF (~85 mL or 77%

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reactor fill) using inert atmosphere Schlenk transfer techniques. The reactor was sealed under an atmospheric pressure flow of nitrogen gas, placed in beaker-shaped custom heating mantle (Glas-Col with an Omega CN4800 temperature controller), and slowly heated with constant stirring using an external magnetic stirrer. The reported reaction temperatures were measured by an internal reactor thermocouple. Typically, the Cu_3N precursors were heated from room temperature to an intermediate temperature (140 °C for toluene and 120 °C for THF). Heating rates included ramping to ~50 °C (1−2 °C/min) and holding at this level for 4 h and then ramping to ~100 °C and holding at this temperature overnight (10−12 h) to facilitate the synthesis of metal azide intermediates. No significant pressure increases above the solvent background were observed at this point. After metal azide formation, subsequent temperature increases in ~5−10 °C increments were made over several days (~40 °C/day for toluene and ~25 °C/day for THF) in order to facilitate moderate (nonexplosive) copper azide decomposition, as indicated by gas evolution rates monitored using the reactor's analogue pressure gauge. Increases in reaction temperature were only made after the vessel pressure had reached a plateau, which usually occurred within a few hours. The maximum reaction temperature was determined as the point where gas evolution ceased, which indicated that all of the copper azide had decomposed. The maximum Cu_3N reaction temperature (185 °C for toluene and THF) was typically maintained for nearly 1 day. The total solvothermal reaction time was 3−5 days and no significant product advantages were observed from longer reaction times.

After the reactor was cooled to room temperature, the headspace gases were sampled by gas-phase IR and the reaction solutions were removed under inert conditions using Schlenk transfer techniques. The as-synthesized solids were dried under vacuum and transferred to an argon-filled glovebox. The sodium chloride byproduct was removed from finely ground samples by dissolution (under N_2 atmosphere) in degassed methanol. Note that a successful alternative sodium chloride removal solvent was glycerol/ethanol solution (50/50 by vol.). The washed solid was filtered using air-free Schlenk techniques, then dried under vacuum, and stored in a glovebox. If after washing residual NaCl was detected by X-ray diffraction, the samples were rewashed with methanol. It is possible to briefly wash the copper nitride product with water, but care must be used to prevent hydrolysis of the small particles.

Selected as-synthesized and washed products were annealed at elevated temperatures (300−350 °C) in sealed, evacuated silica ampules for 1−2 days. These annealing studies were performed to investigate the phase and structural thermal stability of as-synthesized copper nitrides and to determine whether their crystallinity could be improved by annealing. Additional annealing studies were performed in vessels open to the air, to examine oxidative stability.

Experiments to examine the intermediates formed in these copper reactions were performed in either Parr reactors held at temperatures below major decomposition events or on the benchtop using an air-free (N_2 flow) apparatus consisting of a Schlenk flask with a condenser column and heating mantle. In the benchtop reactions, approximate solvent volumes of ~80 mL with 5−7 mmol of $CuCl_2$ and 10−14 mmol of NaN_3 were used.

Safety note: Metal azides are often thermally unstable and shock sensitive. Care should be taken whenever working with reactions that produce azides as products or intermediates. Reactions should be performed on small scales in high-pressure vessels with safety release valves. Use proper protection and extreme caution when working with undecomposed metal azide intermediates. Solid metal azides may detonate upon rapid heating or vigorous grinding and potentially by friction from spatula scraping.

Characterization Methods

The phase and crystallinity of the products were analyzed by powder X-ray diffraction using a Siemens D5000 diffractometer (50 kW, 30 mA, 0.03°/step, and 3−5 s/step count times). An external crystalline silicon powder standard consisting of a finely ground single-crystal silicon wafer (>99.9%) was used as a reference for lattice parameter calculations and crystallite size measurements. Nitride product lattice parameters were determined by least-squares refinement and average crystallite sizes were calculated from several nitride peaks in the 20−50° 2θ region using the Scherrer and Warren equations.[18] Unit cell structures, simulated powder X-ray diffraction patterns, and lattice parameter refinements were generated using Powder Cell 2.3 (http://www.ccp14.ac.uk/) and the POV-Ray 3.1 (www.povray.org) computer programs. Infrared spectra were taken on a Nicolet Nexus 670 spectrometer in transmission mode using KBr pellets for solids or a 10 cm path length cell with NaCl windows for gases. Solution ^1H NMR in C_6D_6 was performed on select reactor solutions after reaction on a Bruker AC 300 MHz spectrometer. Thermogravimetric-differential thermal analysis experiments were performed on a Seiko Exstar TG-DTA 6300 system under flowing argon or compressed air with a 5−10 °C/min heating ramp. Copper and sodium contents were determined quantitatively by inductively coupled plasma (ICP) emission spectroscopy on dilute nitric acid solutions of dissolved products (Perkin-Elmer Plasma 400 Emission Spectrometer). Copper contents were also determined thermogravimetrically by decomposing copper nitride to its elemental state and then oxidizing it to CuO. Bulk elemental CHN combustion analysis was obtained from Desert Analytics (www.desertanalytics.com). Scanning electron microscopy information was obtained with an Hitachi S-4000 field emission system (5 kV, 11 μA) on powders affixed to aluminum or carbon holders. This system includes an IXRF X-ray microanalysis system for energy dispersive spectroscopy (20 kV, 14 μA) that provided semiquantitative information on copper, sodium, and chlorine ratios in the samples. Room-temperature magnetic susceptibility measurements were obtained on a Johnson-Matthey MKS-Auto (Mark II) benchtop magnetic susceptibility balance. Solids probe electron impact mass spectrometry was carried out using a VG TRIO-1 quadrupole mass spectrometer system.

Results and Discussion

Copper Azide Precursor Synthesis and in Situ Decomposition in Toluene. The basic approach to inorganic metathesis (exchange) reactions is similar to that of conventional organometallic Grignard or lithium alkyl reactions. A thermodynamic driving force should exist in order for the reaction to proceed at a moderate temperature. Copper(II) diazides, $Cu(N_3)_2$, are well-studied and their synthesis has generally been accomplished by related exchange pathways, using reagents such as aqueous or ethanolic copper nitrate or copper oxide reactions with HN_3 and NaN_3.[19,20] When using reduced copper(I) salts or reducing conditions, one can produce a less stable lower valent copper(I) azide, CuN_3. In

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the current study, the production of an alkali halide salt, specifically NaCl, provides the enthalpic drive for the formation of a copper azide precursor intermediate (eq 1).

$$CuCl_2 + 2NaN_3 \rightarrow \mathbf{Cu(N_3)_2} + 2NaCl \qquad (1)$$

Generally solvothermal chemical reactions occur most readily when both reagents are soluble. In the current study, $CuCl_2$ is insoluble in toluene at room temperature, but it and partially substituted metal azide intermediates may have increased solubility in toluene at elevated temperatures. The NaN_3 reagent and NaX reaction byproducts are insoluble in toluene, even at elevated temperatures. Thus, these solvothermal reactions are continuously stirred in order to break up NaCl crusts that can form on the NaN_3 microcrystallites, to improve precursor mixing and contact, and to facilitate complete copper azide formation.

The initial stage of these copper nitride reactions involves maintaining temperatures below the point of observable gas evolution above the toluene background for about 1 day to ensure completion of the initial copper azide precursor reaction. The reactor pressure at this point was essentially equal to that observed for the toluene alone, though the low sensitivity of the analogue pressure gauge cannot completely rule out some azide decomposition. Note that metal azides are generally friction-sensitive, so the stir bar may initiate some local azide decomposition. After the copper azide formation stage, the reactor temperature was slowly increased (~40 °C/day) and the internal reactor pressure was monitored as a function of temperature and time. Pressure increases that were significantly above the solvent background were taken as an indication of metal azide decomposition with nitrogen evolution and copper nitride formation (eq 2).

$$Cu(N_3)_2 \rightarrow \mathbf{CuN_x} + (3 - 0.5x)N_2 \qquad (2)$$

The reactor temperature was raised to facilitate the slow evolution of N_2 and avoid a rapid copper azide decomposition process. The superheated toluene (bp = 111 °C) acts to moderate metal azide decomposition, and when the system temperature was cautiously raised (~5−10 °C increments), explosive events were not observed in these systems. Visible pressure evolution is apparent by ~160 °C, somewhat consistent with the reported thermal properties of solid $Cu(N_3)_2$ that explosively decomposes near 200 °C.[19] For comparison, a late transition metal azide, AgN_3, decomposes explosively at 230 °C in the solid state;[19] however, it decomposes slowly at 190 °C under solvothermal (toluene or THF) conditions to produce elemental silver particles.[21] The maximum reaction temperature for copper azide decomposition in toluene was determined as the point where the observed pressure increase after raising the reactor's temperature is primarily due to toluene vapor and existing evolved gases. The maximum temperature for the copper azide decomposition in toluene was 185 °C and is within 40 °C of the approximate azide decomposition onset temperature. The maximum temperature was maintained for nearly 1 day to ensure that any residual azide was decomposed. For the nearly 30 mmol toluene reaction, the generated gas pressure at 180 °C was nearly 600 psi more than the toluene vapor pressure background (~150 psi). A comparison of pressure generation versus temperature will be discussed later.

Analysis of Copper Nitride Synthesis from Toluene. After the reactor was cooled to room temperature, the internal gas pressures were lower than those calculated based on quantitative yields of N_2 gas assuming that an ideal gas occupies the free volume of the reactor (~40 mL). This is not surprising since most of the reactor contains a solvent (~85 mL) with gas dissolution ability. After depressurizing the reactor, evanescent bubbles were routinely observed to evolve from the toluene solution. IR analysis of the pressurized gas in the reactor was consistent with mainly toluene, but ammonia was also detected in the reactor headspace. Since azide decomposition likely occurs via reactive nitrene intermediates, some of these reactive Cu−N species may abstract protons from the solvent and produce amine intermediates that are eventually released as NH_3.[22] Additionally, the copper azide reaction in toluene shows gas-phase IR evidence for a volatile (possibly organic) azide (~2200 cm^{-1}), suggesting side reactions with the solvent may occur before azide decomposition. While the toluene solution discolors to an orange-brown color after the solvothermal reaction, its IR spectrum and ^1H NMR were still consistent with primarily toluene.

The solid product from the copper azide decomposition reaction was isolated, washed with methanol to remove NaCl and any unreacted starting materials, dried under vacuum, and transferred to an inert atmosphere glovebox. The NaCl byproduct was initially removed using a glycerol−ethanol solution; however, it was later observed that methanol works equally well and does not coat the product particles with organic residues to the extent that glycerol does. For this reason, methanol was the primary solvent used for NaCl removal. Powder X-ray diffraction (XRD) analysis of the copper azide decomposition product prior to methanol washing shows crystalline cubic NaCl and small cubic Cu_3N peaks (Figure 1a). After NaCl is washed away, the XRD scan of the dark brown solid shows a simple cubic structure consistent with Cu_3N (JCPDS file # 2-1156, anti-ReO_3 structure) as the only crystalline material observed (Figure 1b).

A Solvent Comparison: Copper Azide Formation and Decomposition in THF. In our previous work on the gallium azide[17] and silver azide[21] systems, switching toluene for a coordinating cyclic ether, tetrahydrofuran (THF, bp = 82 °C), did not alter overall solvothermal reaction significantly, but it did change product morphologies and increased dissolution of NaCl byproduct *during* the reaction. As noted above, the reagents and products are all insoluble in toluene reaction, but $CuCl_2$ is soluble in THF and the NaCl byproduct is soluble in THF at elevated temperatures. These two

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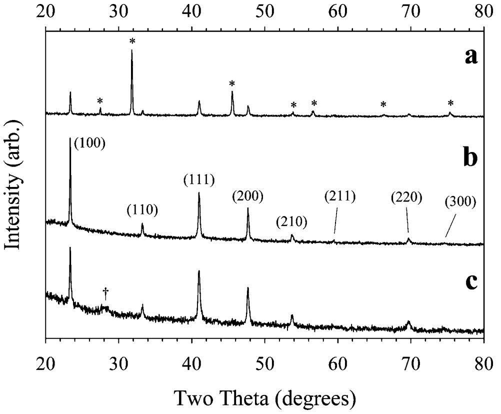

Figure 1. Powder X-ray diffraction of the solvothermal decomposition products from the reaction of $CuCl_2$ and NaN_3 in toluene at 185 °C (a) as-synthesized [NaCl peaks noted with an *] and (b) after washing with methanol [cubic Cu_3N peaks marked with (*hkl*) indices] and (c) a methanol-washed product from the reaction of $CuCl_2$ and NaN_3 in THF at 185 °C [† marks an unidentified species].

considerations suggest that the azide formation and decomposition processes may be more facile in the THF solvothermal medium.

An initial THF reaction attempt (50 °C/h heating to ~150 °C) produced a fairly rapid decomposition event that generated significant pressure and transient solution heating above that provided by the mantle. This event was likely due to rapid initial heating that produced a densely packed and unstable copper azide solid without any NaCl byproduct since NaCl should be dissolved in THF. Alternatively, a soluble $Cu(N_3)_2$−THF adduct may have formed that had lower thermal stability than a solid $Cu(N_3)_2$. XRD analysis of the solid recovered from this reaction reveals that rapid heating/decomposition produced mainly Cu metal, along with a small amount of Cu_3N.

When the THF reaction was repeated with slower initial heating and at half the reagent scale of the toluene synthesis, the solvothermal decomposition process was moderate and qualitatively similar to that using toluene. Detectable gas evolution was evident at ~130 °C and the reaction was heated to a maximum of 185 °C. After the reaction was cooled to room temperature, the headspace gas above the solution contained traces of NH_3. The methanol-washed product showed evidence of crystalline cubic Cu_3N (Figure 1c). When the THF reaction was repeated and held at the 185 °C for 1 day longer, small Cu impurity peaks were also observed by XRD in addition to Cu_3N, indicating slow product decomposition under extended solvothermal heating.

The THF reaction was also run at a lower maximum temperature (~160 °C) and a much less crystalline Cu_3N product was isolated, but without evidence of crystalline Cu. After this lower temperature reaction, the THF solution had a dark green coloration, characteristic of dissolved copper salts or unreacted $Cu(N_3)_2$. Crystals of $Cu(N_3)_2$ have been previously described as green-black in color.[23] When the green solution was isolated, a fine green powder slowly settled out, leaving behind a light green solution and both the solid and solution showed evidence of azide IR vibrations near 2050 cm^{-1}. The green solid also showed XRD evidence of NaCl, but no crystalline copper azides. Note that a light green solution was also observed in the short duration, but not the longer duration THF reactions at 185 °C described above.

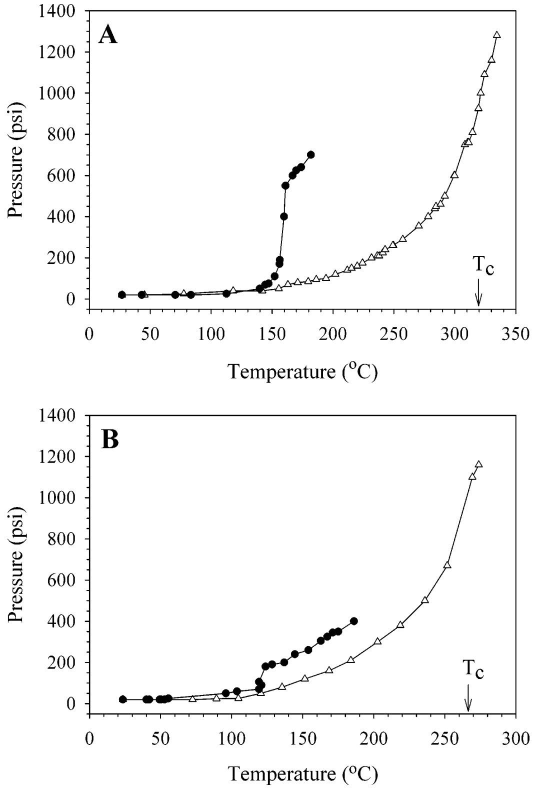

Figure 2. A comparison of reactor gas pressure versus temperature curves (A) for toluene alone (triangles) versus toluene solvothermal reactions of $CuCl_2$ with NaN_3 (circles) and (B) for THF alone (triangles) versus a THF reaction of $CuCl_2$ with NaN_3 (circles). The pure solvent critical temperatures (T_c) are noted.

Pressure Evolution during Cu_3N Formation Reactions. From pressure monitoring data, it is clear that copper azide decomposition in THF begins at lower temperatures than in toluene. The graphs in Figure 2 plot the reactor pressure versus internal temperature for the toluene and THF copper azide decomposition reactions. Background experiments with pure solvent are included for comparison. These curves demonstrate that copper azide decomposition onsets are somewhat dependent on the solvent, with the toluene onset (Figure 2A) occurring about ~30 °C higher than THF (Figure 2B). The lower decomposition temperature in THF may be due to a higher degree of copper azide solid aggregation as a result of byproduct NaCl dissolution and friction (stir bar) initiated metal azide decomposition. Alternately, soluble and thermally unstable THF coordinated copper azide intermediates may be generated.

The solvothermal reactions conducted in this study were at temperatures below the critical points of the respective solvents with critical temperatures (pressures) of 267 °C (753 psi) and 319 °C (597 psi) for THF and toluene, respectively. Notice how the curves in Figure 2 become clearly nonlinear near the critical temperatures. Finally, Figure 2 does not include any temporal decomposition data. For example, the

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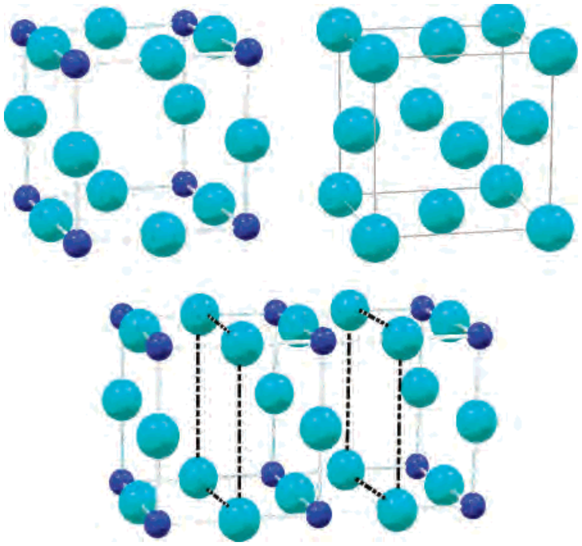

Figure 3. Unit cell structure comparison for cubic Cu_3N (top, left) and cubic copper metal (top, right); alternate view of two Cu_3N unit cells emphasizing partial fcc Cu arrangement (bottom). Legend: light blue = Cu, dark blue = N.

thermal degradation of unstable copper azides in toluene and THF reactions seems to occur at very different relative rates. When $Cu-N_3$ test reactions were held at a 120 °C internal temperature, visible pressure evolution was apparent in the THF reactor within an hour, whereas toluene required more than 1−2 days before showing any pressure rise. In the latter reaction, starting materials and some Cu_3N were evident by XRD in the isolated solid. A more detailed examination of reaction intermediates is discussed later in this article.

Copper Nitride Product Analysis. The cubic Cu_3N structure is built up by corner-sharing NCu_6 octahedra with N−Cu−N bond angles near 180° (Figure 3). It has as an inverse ReO_3 structure with one Cu_3N per unit cell (cubic, *Pm*3*m*, $a = 3.815$Å, density = 6.1 g/cm^3) and is less dense than the elemental copper face-centered cubic structure with 4 Cu atoms per unit cell shown in Figure 3 ($a = 3.61$ Å, density = 9.0 g/cm^3). The Cu−N bond lengths in Cu_3N are 1.91 Å, which is much closer to the sum of covalent Cu and N radii (1.87 Å) versus the sum of ionic Cu^+ and N^{3-} radii (2.67 Å). For further comparison, Figure 3 also shows an extended version of the Cu_3N structure (2 unit cells along the *b* axis), showing that it could be thought of as a partial fcc Cu cube with Cu atoms missing from the center of the *ac* faces and N in all octahedral holes on the cell edges of the *ab* faces.

Electronic structure calculations predict that Cu_3N should exhibit diamagnetic properties[24] and have a small semiconducting band gap (∼0.5 eV), though thin films with a larger band gap (1.65 eV) have been reported.[11b] Theoretical studies also show that placing additional Cu atoms in the Cu_3N body center may lead to metallic behavior.[24] In the fully ionic limit, Cu_3N is comprised of Cu^+ (d^{10}) metal cations and N^{3-} anions and should have diamagnetic properties. Our room-temperature magnetic susceptibility of the crystalline copper nitride product from toluene verifies that the washed Cu_3N powder is diamagnetic ($\chi_m = -8.6 \times 10^{-6}$ emu/mol at 298 K). Future studies will examine the feasibility of adding other metals into the body center of the Cu_3N structure during the solvothermal reaction, forming perovskite (ABX_3) type structures and altering the material's magnetic properties.

A variety of structure and characterization data on copper nitride solvothermal syntheses and products are compared in Table 1. The cubic unit cell lattice parameters are consistent with previous literature reports and the XRD crystallite sizes of each of these metal nitrides are in the sub-50 nm region. Notably, the average crystallite sizes for the THF reaction products are nearly 20% smaller than those from toluene. No specific experimental controls were used to target size control in these metal nitride reactions; however, studies with mixed solvents and coordinating additives are underway as particle size control strategies during metal azide synthesis and decomposition.

Solid-state IR of the washed Cu_3N from toluene shows small peaks consistent with organic C−C and C−H molecular vibrations likely due to surface sites capped with tolyl groups or alcohol species. There are also sharp Cu−N lattice phonon vibrations with fine structure at ∼650 cm^{-1} (Figure 4a), which is also in the region of Cu−N symmetric stretches identified in $Cu-N_3$ systems.[25] The sharpness of these peaks and presence of an azide stretching peak at ∼2050 cm^{-1} suggests that one or more of the sharp transitions in the 600−800 cm^{-1} region may be due to surface $Cu-N_3$ bonds. The equivalent washed Cu_3N sample from THF shows slightly more intense organic/solvent peaks and a broader, less resolved Cu−N lattice vibration (Figure 4b). This provides some evidence that the coordinating solvent, THF, binds more readily to the nitride particle surfaces. Solids probe electron impact mass spectrometry data on the washed Cu_3N products show clear evidence for intact THF (71 amu) loss from the THF product, while the toluene product shows toluene desorption in addition to benzene and aminotoluene fragments. The latter signal indicates that covalent $Cu-NH_x-CH_y-(C_6H_5)$ bonds may be present on the particle surfaces.

Compositional Analysis of Cu_3N Products. Energy dispersive spectroscopy (EDS) on washed Cu_3N powders showed that Cu is the major atomic sample constituent and sodium was below baseline detection limits, which is significant because alkali metals have precedence for incorporation into late transition-metal nitrides.[3,7] Chlorine contents were barely detectable in the toluene reaction product (<0.6 wt %) and nearly 2.5 wt % in the THF product. The copper and sodium contents were quantified using ICP analysis, which shows that Na is less than 0.3 wt % in all washed products. Copper was also examined by a two-step thermogravimetric-differential thermal analyses (TG-DTA) experiment where Cu_3N was decomposed in argon at 500 °C and then subsequently oxidized in a dilute stream of oxygen (CuO

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Table 1. Synthetic and Structural Data for Copper Nitride Reactions and Products

nitride product	max. temp/ solvent	yield/ color[a]	XRD unit cell parameter	crystallite size (XRD)	composition| Cu^b:N:C:H (wt %)
Cu_3N	185 °C toluene	85% black	$a = 3.817(5)$ Å	30(6) nm	67.1(70.8):14.08:11.74:0.65
Cu_3N	185 °C THF	98% brown	$a = 3.816(5)$ Å	24(2) nm	53.7(58.6):22.50:12.43:1.05

[a] Based on ideal reaction assuming all copper reagent forms Cu_3N after washing. [b] Cu from ICP analysis. TGA oxidation result is in parentheses.

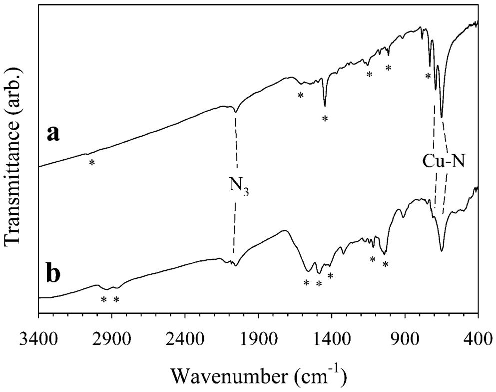

Figure 4. Comparison of IR data for methanol-washed products from Cu_3N synthesized in (a) toluene and (b) THF. The * indicates likely positions for solvent-based vibrations.

confirmed by XRD). This two-step process was required because direct Cu_3N oxidation was too vigorous to obtain accurate weight change data. The data in Table 1 show that the results from ICP and TGA methods are similar.

A constant challenge in solvothermal syntheses is that organic substituents often remain coated or bonded to the particle surfaces. TGA experiments with washed Cu_3N in an argon flow below 275 °C show weight losses attributed to surface organic and azide residues consisting of ∼10−15 wt % of the sample. Combustion bulk elemental analysis (C−H−N) was utilized to aid in determining the overall bulk chemical composition of the synthesized nitrides (Table 1). For comparison, the ideal weight percent nitrogen for Cu_3N is 6.8%. When equivalent toluene and THF Cu_3N samples were dried under flowing argon at 250−270 °C prior to elemental analysis, they had lower CHN contents compared to those in Table 1; specifically the Cu:N:C:H values (wt %, Cu from TGA data) for toluene samples were 78.3:9.60: 5.53:0.18 and for THF samples were 61.7:21.72:12.30:0.87. While greater than 90% of the sample mass was determined, it is clear that the THF products contain significantly more organic and amino or chloro content than the toluene samples. Based on these data, some THF may decompose during the nitride reaction to form a solid organic, possibly polymeric, byproduct. An organic component could account for the small broad unidentified XRD peak at ∼28° in Figure 1c, which is not coincident with any likely copper species.

In general, it appears that the more poorly coordinating solvent (toluene) leads to more crystalline and contaminant-free Cu_3N (less excess C, H, N). One potential reason for this is that aggregated $Cu(N_3)_2$ solids decompose efficiently to the Cu_3N product structure. The solid-state structure of $Cu(N_3)_2$ contains a distorted octahedral CuN_6 geometry, similar to the Cu_3N product.[23] The more Lewis basic solvent, THF, may enhance copper azide dissolution, allowing the decomposing azides to react with solvent to form terminal amines or over-reduce to metallic Cu, prior to bonding to other decomposing copper azides to form the Cu_3N extended structure.

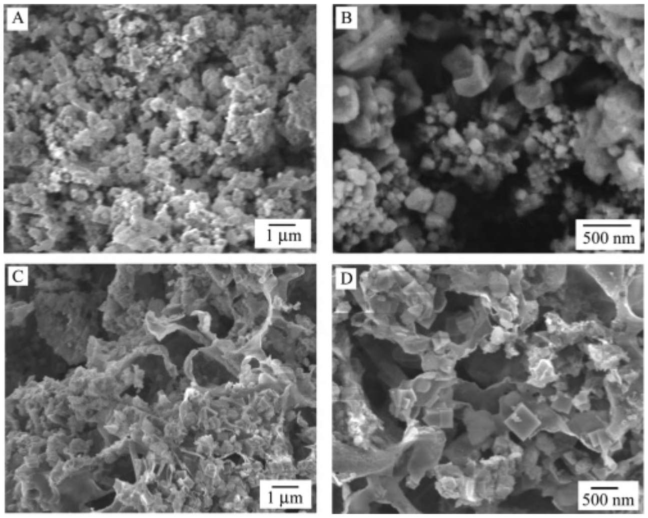

Figure 5. Scanning electron microscopy images of Cu_3N products from copper azide decomposition in toluene (A, B) and in THF (C, D).

Copper Nitride Particle Morphologies. The Cu_3N powders from toluene are recovered as finely divided powders, while the product from THF was mainly recovered as a fused mass on the bottom of the reactor with some product formation on the reactor walls. The latter observation suggests that some soluble azide precursors were formed and decomposed on the walls. One major synthetic difference in the current study, as compared to our previous solvothermal nitride studies, is constant stirring with a coated stir bar that serves to break up larger aggregates and promote reagent mixing. The isolated copper nitride morphologies as determined by scanning electron microscopy (SEM) are submicrometer-sized aggregates (∼0.5−1 μm) of smaller faceted particles (∼50 nm), some with nearly cubic shapes (Figure 5A,B). It is not surprising that the products from the solvothermal toluene decomposition are highly aggregated. The poorly coordinating nature of the solvent will encourage copper azide crystallite aggregation prior to decomposition, resulting in closely associated Cu_3N crystallites.

The Cu_3N product from THF has a less well-defined microstructure. There are wide areas of aggregation, separated by irregularly shaped voids (Figure 5C). This morphology has similarities to our previous THF solvothermal studies. The solvent dissolves NaCl, and when it recrystallizes upon cooling, the product powder may settle and aggregate around these salt crystals. Upon washing, voids from the salt crystals presence would remain. In addition, since NaCl is soluble during the reaction, the as-formed Cu_3N particles are likely in intimate contact in the reactor and may readily fuse together during the reaction, forming the

Table 2. Characterization of Intermediates in $\mathrm{CuCl_2/NaN_3}$ Benchtop Reactions

max temp (hold)[a]	XRD species[b] (in decreasing intensity)	solid IR data ($\mathrm{cm^{-1}}$, intensity, shape)
	Toluene Reactions	
103 °C (18 h)	$\mathrm{NaN_3}$ > $\mathrm{CuCl_2}$ > **NaCl** ≈ *CuCl* > $\mathit{Cu(N_3)_2}$	Cu−N (636, strong, sharp) $\mathrm{N_3}$ (2090−2100, strong, broad)
113 °C (1 day)	*CuCl* > **NaCl** ≈ $\mathrm{NaN_3}$ > $\mathrm{CuCl_2}$ > $\mathit{Cu(N_3)_2}$	Cu−N (635, weak, sharp) $\mathrm{N_3}$ (2059−2151, strong, broad)
113 °C (2 day)	*CuCl* > **NaCl** > $\mathrm{NaN_3}$ > $\mathit{Cu(N_3)_2}$	Cu−N (639, strong, sharp) $\mathrm{N_3}$ (2079−2120, strong, broad)
113 °C (3 day)	**NaCl** > *CuCl* >$\mathrm{NaN_3}$ > $\mathit{Cu(N_3)_2}$	Cu−N (∼570, weak, broad) $\mathrm{N_3}$ (2059−2151, strong, broad)
	Xylene Reactions	
116 °C (14 h)	*CuCl* > $\mathrm{NaN_3}$ > $\mathit{Cu(N_3)_2}$ > **NaCl**	Cu−N (639, strong, sharp) $\mathrm{N_3}$ (2105, strong, broad)
118 °C (1 day)	**NaCl** > $\mathit{Cu(N_3)_2}$ > $\mathit{CuN_3}$	Cu−N (∼610, weak, sharp) $\mathrm{N_3}$ (2039−2130, strong, broad)
125 °C (18 h)	**NaCl** > $\mathit{Cu(N_3)_2}$ > $\mathit{CuN_3}$ > $\mathbf{Cu_3N}$	Cu−N (∼630, weak, sharp) $\mathrm{N_3}$ (2039−2130, strong, broad)
135 °C (1.5 day)	**NaCl** > $\mathbf{Cu_3N}$	Cu−N (652, strong, sharp) $\mathrm{N_3}$ (2059−2130, strong, broad)

[a] Sequential heating of same reactant solution (toluene or xylene). Each reaction was ramped to maximum temperature over ∼1 day, held there for the time indicated in parentheses, and then cooled to room temperature for sample extraction and analysis. [b] Code: starting materials = regular type, intermediates = italic type, and products = bold type.

continuous structures shown in Figure 5C. Closer examination of other regions of the THF-synthesized Cu_3N shows an irregular aggregate and cubelike structures similar to that from toluene (Figure 5D).

The cubic faceting observed for some Cu_3N particles could give rise to some preferred orientation effects that are sometimes observed in powder diffraction data. In several Cu_3N samples, the (100) XRD peak has significantly increased intensity from that expected from a homogeneous and random distribution of crystallites. Several attempts were made to model this to different atom positions and distributions in a cubic unit cell, but no alternate structure was found to account for the intensity differences. The most probable scenario is that the Cu_3N crystallites have a preferred (100) orientation on the XRD sample slide. This could be the case if the crystallites have cubic habits that follow the unit cell edges. Previous studies showed that physically deposited Cu_3N films frequently grow with a (100) preferred orientation.[11,12] In addition, repeated grinding of our Cu_3N toluene sample leads to a slight decreases in the (100) peak intensity relative to the other XRD peaks.

Copper Nitride Thermal Stability. Washed Cu_3N samples are stable in air at room temperature for at least 1 year, but rapidly oxidize to CuO when heated in air above 300 °C and decomposes to elemental Cu upon moderate heating in inert conditions. From TG-DTA in argon (10 °C/min ramp), Cu_3N from toluene decomposes by ∼440 °C, while samples produced in THF decompose at lower temperatures (∼360 °C). These decomposition values are temperature-, environment-, and time-dependent since isothermal TGA studies on the toluene Cu_3N product show that it converts to Cu metal after several hours in flowing argon at 350 °C. Similarly, washed samples heated in evacuated ampules at 300 °C overnight lead complete decomposition of the THF sample to Cu metal with no evidence of copper oxides (i.e., no coordinated THF supplies oxygen), while the toluene product heated under identical conditions resulted in a ∼50:50 mixture of Cu_3N and Cu.

The differing thermal stability of THF and toluene products may be a result of crystallite/particle sizes and amount of bound organic agents that could act as advantageous reducing agents. The more poorly coordinating solvent, toluene, produces a particle morphology that is more visibly homogeneous than that from the more coordinating THF, with its glassy and faceted regions. Up to the decomposition point, no appreciable changes in crystallite size or particle morphology were observed, demonstrating that the copper nitride crystallite and particle size are significantly determined during the solvothermal copper azide decomposition process. We do not know whether the dispersion of the metal azide intermediate is a major factor affecting the nitride crystallite size or particle morphology, but the coordinating ability of the solvent, the stirring speed, and azide decomposition rate all likely play important roles in this regard.

Probing Intermediates in Copper Azide to Nitride Solvothermal Reaction. In our earlier GaN work, energetically unstable polymeric metal azide solids were postulated as likely intermediates[17] and there is evidence for such structures from other synthetic studies.[26] For safety reasons, metal azide intermediates were generally not isolated in our earlier solvothermal azide to nitride studies. However, a copper azide reaction in toluene performed in a Parr reactor was stopped at 125 °C and the isolated solid product showed strong $Cu-N_3$ IR evidence (2062 and 1447 cm^{-1}) and the XRD showed the presence of crystalline CuN_3, in addition to NaCl and Cu_3N. These results show that, before 130 °C, our postulated primary "$Cu(N_3)_2$" precursor (eq 1) has already begun to decompose to a reduced copper(I) azide and some copper(I) nitride product. There is literature reference to Cu(II) to Cu(I) azide conversion in heated solutions[19] and CuN_3 is also a thermally sensitive compound, rapidly decomposing upon heating to 200 °C.[27]

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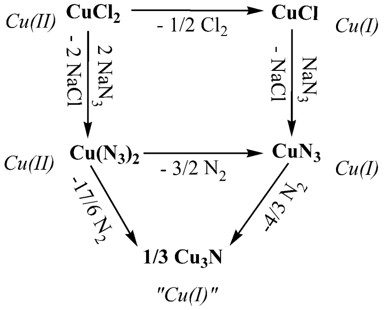

Figure 6. Proposed chemical pathways for solvothermal copper azide to Cu_3N formation based on IR and XRD analysis of solvothermal reaction intermediates shown in Table 2.

This surprising result led to a more systematic examination of intermediates in the Cu−N_3 system using IR and XRD analysis of reaction aliquots from benchtop solvothermal reactions in refluxing toluene (bp 111 °C) and refluxing xylene (bp 139 °C). The refluxing toluene reaction reached internal temperatures of ∼113 °C and portions of the solid slurry were sampled over the course of several days. Table 2 shows the progression of XRD species and diagnostic IR peaks for aliquots taken during this experiment. There is clear evidence for formation of reduced Cu(I) intermediates, CuCl and CuN_3, in addition to starting materials and $Cu(N_3)_2$ and NaCl as predicted by eq 1. Even after 6 days of sequential heating, there was no evidence of crystalline Cu_3N from this ambient pressure toluene test.

m-Xylene (dimethylbenzene) was chosen a close structural relative of toluene with a higher boiling point. The xylene reaction study was run with internal solvent temperatures ranging from 116 to 135 °C. The XRD and IR of solid aliquot species are listed in Table 2. Once again the reduced CuCl appears along with $Cu(N_3)_2$, and then as time and temperature increase, CuN_3 is dominant. Finally, the xylene data show clearly that Cu_3N begins to form as the Cu-azide intermediates disappear. Taken as a whole, these data provide evidence for a potential dual pathway route to Cu(I) nitride materials from Cu(II) and in situ generated Cu(I) azide precursors. Figure 6 diagrams a progression of copper species that is consistent with the results in Table 2. The reduced $Cu(N_3)$ may form from prereduced CuCl or from reductive degradation of $Cu(N_3)_2$. Either pathway could lead to Cu_3N after azide decomposition.

Conclusions

The solvothermal reaction of copper(II) chloride and sodium azide in nonaqueous superheated toluene or THF leads to copper azide intermediates that decompose to nanocrystalline copper nitride at moderate temperatures. Thermally metastable cubic Cu_3N is produced by moderating the azide decomposition through controlled heating regimens at temperatures below 200 °C. The crystalline nitride products have nanoscale crystallite and particle sizes, with significant aggregation and modest thermal stability ($<$350 °C). Surprisingly, the toluene system with insoluble reagents and intermediates produced more crystalline Cu_3N with fewer detected impurities, compared to the more Lewis basic and coordinating solvent (THF). This suggests that metal azide to metal nitride conversions may work best as a moderated solid−solid conversion rather than a conventional dissolved single-source precursor solution decomposition reaction.

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