A Solid-State Metathesis Route to $MgSiN_2$

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Nitrides, such as magnesium silicon nitride, hold promise for applications requiring materials with high thermal conductivity. The synthesis of the ternary nitride $MgSiN_2$ is accomplished using SiO_2 and Mg_3N_2 as reactants in a solid-state metathesis (exchange) reaction. This self-propagating reaction is readily initiated when a flame with a temperature ≥1100 °C is brought into contact with a pressed SiO_2/Mg_3N_2 pellet. By using Mg_3N_2 in ≥1 M excess, X-ray-pure $MgSiN_2$ can be produced. With lower ratios, elemental silicon forms as an impurity. Increasing the flame initiation temperature to ≥2500 °C can also be used to eliminate silicon impurities with the benefit of increasing the crystallinity of the product. The use of other forms of silica as a silicon source provides an inexpensive alternative to produce $MgSiN_2$. A variety of silica sources are examined, including fumed silica, sand, ground quartz, bottle glass, and rice hull ash. Since rice hull ash is an industrial waste product from rice processing, new applications such as in the synthesis of $MgSiN_2$ could prove to be environmentally friendly.

Introduction

As integrated circuits shrink while their component density increases, the need for improved thermal management substrates becomes increasingly important. To meet this challenge, more thermally conductive materials must be developed to aid in heat dissipation. Currently, ceramics such as alumina are used in integrated circuit packaging. Other excellent thermal conductors include, aluminum nitride and boron nitride; however, their synthesis and processing make them prohibitively expensive. Currently, the material that is most widely used in integrated circuits is optimized alumina (Al_2O_3). Depending on the processing parameters, alumina possesses a thermal conductivity ranging from 17 to 38 W m^{-1} K^{-1}.[1]

Substituted silicon nitrides have attracted attention as alternative thermal conductors.[2−5] Of these, $MgSiN_2$ is one of the most promising, since an unoptimized compacted powder has a thermal conductivity (25 W m^{-1} K^{-1})[1] comparable to that of optimized Al_2O_3. A real problem is finding an inexpensive route to $MgSiN_2$. The synthesis of $MgSiN_2$ has been carried out by heating Si_3N_4 with either Mg_2Si or Mg_3N_2 at 1200 °C for several hours under nitrogen.[6] This process requires a significant input of energy to obtain the desired phase. The use of Si_3N_4 further complicates the synthesis, since this material is both energy intensive and relatively expensive to produce. Other methods, such as single-source precursors to Si_3N_4, have been developed, but they also require significant energy input.[7,8]

Solid-state metathesis (SSM) reactions offer a method to access compounds that are often difficult to produce conventionally. This technique has shown promise in the rapid synthesis of a wide range of crystalline refractory ceramics[9−11] and other inorganic solids.[12−15] Solid-state metathesis reactions can be used to produce high-quality solid solutions and ceramic composites[16] as well as to control crystallite size.[17] Recently, SSM reactions have been used to form main group nitrides such as aluminum nitride,[18] and Mg_3N_2 has been successfully utilized as a nitriding agent for the synthesis of transition-metal nitrides.[19−22] The synthesis of $MgSiN_2$

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through SSM reactions could provide a straightforward, rapid method for its production. Here we demonstrate that readily available precursors, SiO_2 and Mg_3N_2, can be used to produce $MgSiN_2$; reactions involving these precursors differ from traditional SSM reactions in that significant heat input is needed for initiation. This is accomplished using an oxygen/methane torch with a flame temperature of ≥2500 °C. The $MgSiN_2$ product is characterized using X-ray powder diffraction, scanning electron microscopy, energy-dispersive X-ray analysis, and thermal gravimetric analysis.

Experimental Section

Chemicals. The reagents magnesium nitride (Cerac, 99%, 200 mesh), silicon monoxide (Aldrich, ~325 mesh), mineral quartz (X-ray-pure), ammonium chloride (Baker, 99.7%), washed sea sand (Fisher), and sodium amide (Alpha-Aesar, 96%) were used as received. Fumed silica with a surface are of 400 m^2/g (grade S-17, Cabot Corp.) was dried in a drying oven at 180 °C (which returns it to its initial packaged water content of 1.0−1.5 wt %)[23] and stored in a helium-filled glovebox. The ground bottle glass was prepared by grinding glass in a ball mill with alumina grinding pellets. The ground material was then put through wire screens to obtain −325 mesh powder and stored under helium. Rice hull ash (Uncle Ben's, a subsidiary of Mars, Inc.) was dried in an oven at 180 °C, ground, passed through a 325 mesh screen, and stored in a helium-filled glovebox. Diatomaceous earth (Kem-Tek) was dried at 180 °C and stored in a helium-filled glovebox. All other reagents were used as received.

Synthesis. The synthesis of $MgSiN_2$ was carried out by weighing stoichiometric amounts of a silicon source (fumed silica, silicon monoxide, sand, quartz, bottle glass, diatomaceous earth, or rice hull ash) and magnesium nitride in a helium-filled glovebox. The operations were carried out in the drybox to reduce exposure of the powder to atmospheric oxygen and water. Typically about 0.65 g of material was used for each reaction. The reaction mixture was transferred to a 20 mL borosilicate glass scintillation vial, tightly capped, and removed from the glovebox. In air, the powder was quickly transferred to a 0.5 cm diameter die and pressed into a pellet under a load of 5000 lb. The pellet was removed from the die and placed on an alumina block. Typical transfer times were kept to under 1 min to minimize atmospheric interaction with the Mg_3N_2 starting material. The reaction was initiated by heating the pellet with an oxygen/methane torch. A National Torch type 3A blowpipe with a no. 2 tip was utilized for oxygen/methane and hydrogen/oxygen flames. The flame was adjusted to produce a blue cone about 0.75 in. in length. To maintain consistency, the tip of this cone was used to heat the reaction. The pellet was heated on one side until red hot, flipped, and heated to the same point on the other side. Oxygen/acetylene torch initiation was performed using an oxygen/acetylene torch with a no. 0 tip. The flame was adjusted to approximately 4 in. in length. There was no need to flip the pellet when heated with the oxygen/acetylene flame. *Caution! The use of open flames with reactive compounds can be potentially dangerous. Care should be used when undertaking this synthesis.* The reacted pellet was ground under 6.0 M HCl and stirred for 1 h. The product was isolated by two subsequent washes with distilled water, followed by centrifugation, and drying in a hot (180 °C) oven.

Air and flame-free reactions were performed by pressing the reaction mixture into a pellet in a He-filled glovebox. This pellet was then transferred to a mullite tube with a closed end and held under either vacuum or nitrogen. The reaction was initiated by thrusting the tube containing the pellet into a 1450 °C furnace with SiC heating elements (Applied Test Systems) and removing it after 10 min. The reaction was also initiated in an open mullite tube by applying heat in a similar manner.

Microwave Synthesis. Reactions initiated by microwave energy were carried out with a 500 W Panasonic household microwave oven (2.45 GHz) with an alumina disk as the reaction platform. In a He-filled glovebox, reaction mixtures were placed in a tightly capped 20 mL borosilicate vial. The mixtures were then removed from the glovebox, pressed into a pellet under 5000 lb of load, and placed in a quartz tube open to air inside the microwave cavity. Microwave energy was applied at the 100% power setting for 2−3 min.

Amide Wash. Synthesized $MgSiN_2$ was washed in molten sodium amide by using a 1.0:5.0 mass ratio of $MgSiN_2$ to $NaNH_2$. The $NaNH_2$ was loaded into a graphite crucible in a He-filled glovebox. The crucible was resistively heated to 275 °C to melt the $NaNH_2$. The $MgSiN_2$ was slowly added with stirring to minimize the foaming that occurs upon addition of the nitride. The crucible was covered with an aluminum disk and held at that temperature for 5 h. The crucible was cooled and removed from the glovebox. The mixture was carefully rinsed with water. *Caution! $NaNH_2$ reacts vigorously with water, and care should be taken to prevent explosive decomposition.* The $MgSiN_2$ was isolated from the resulting solution by centrifugation and two further washes with water.

XRD Analysis. The products were analyzed using a Crystal Logic $\theta-2\theta$ powder X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Product samples were scanned from $2\theta = 10°$ to $2\theta = 100°$ at 0.1° intervals with a 3 s count time per interval. The patterns obtained were analyzed and interpreted using the Macintosh software MacDiff (http://www.geol.uni-erlangen.de/html/software/Macdiff.html).

Energy-Dispersive Spectroscopy. Semiquantitative analysis was conducted using energy-dispersive spectroscopy (EDS) performed on a Cambridge Stereoscan 250 scanning electron microscope. Analysis was conducted using a Kevex Sigma system equipped with a Kevex super beryllium window (5 μm thick).

Thermal Analysis. Thermogravimetric analyses (TGA; TA instruments model 2950) were performed on washed products. Each sample was loaded onto a platinum pan and heated in air. Differential thermal analyses (DTA) were performed on a Perkin-Elmer Diamond TGA/DTA system. Reactions were studied by compacting the reagents into a 0.125 in. pellet. The pellet was loaded onto the DTA pan, and an alumina cover was loosely placed over the reaction pellet. The analyses were performed under argon.

Hot Pressing. Material prepared from the reaction with a SiO_2:Mg_3N_2 ratio of 1.0:2.0 was pressed in a hot uniaxial press (Materials Research Furnaces, Inc. model H-4.5x7-G-2000-V&G). The material was loaded into a 12 mm graphite die and held at 1550 °C for 2 h under an applied pressure of 87 MPa.

Thermal Conductivity. A pellet 12 mm in diameter and 2.25 mm thick was used for thermal conductivity measurements. The thermal conductivity was measured by using a modified guarded hot plate method.[24] A sample of pure molybdenum (with a thermal conductivity of 138 $W\ m^{-1}\ K^{-1}$) was used as a reference material.

Volume Resistivity. A pellet 12 mm in diameter and 2.25 mm thick was sandwiched between two copper plates. The resistance

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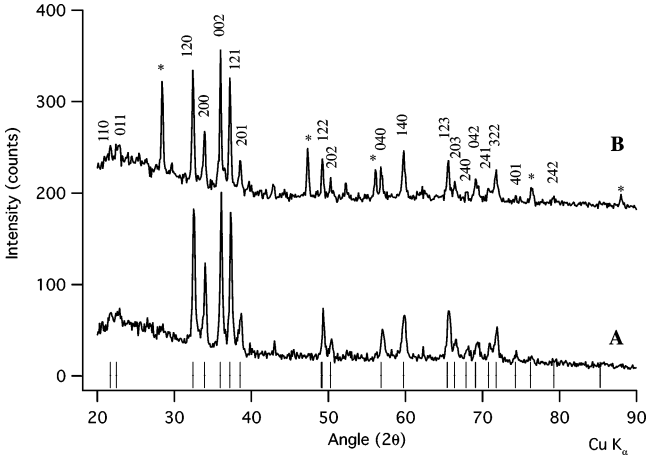

Figure 1. Powder X-ray diffraction patterns of $MgSiN_2$ produced from (A) 1.0:2.0 and (B) 1.0:1.0 ratios of SiO_2 to Mg_3N_2. The Miller indices for $MgSiN_2$ are given above the peaks in (B). The peaks marked with an asterisk in (B) are due to silicon. A simulated stick pattern for orthorhombic $MgSiN_2$ is given below (A).

was measured using a General Radio Co. type 1862-C megohmmeter. The resulting number was used to derive the volume resisitivity.

Results

Reagent Ratios. The ideal $MgSiN_2$-forming reaction (eq 1) utilizes a SiO_2:Mg_3N_2 ratio of 1.0:1.0. This was used as a starting point for investigating

$$SiO_2 + Mg_3N_2 \rightarrow MgSiN_2 + 2MgO \qquad (1)$$

$MgSiN_2$-forming reactions. Reactions were performed with SiO_2:Mg_3N_2 molar ratios varying from 1.0:1.0 to 1.0:4.0. All reactions produce $MgSiN_2$ in varying degrees of quality. The reaction is not very energetic. When the reaction is initiated, the pellet glows red and streams of gas are emitted. The isolated product does not exhibit any melt morphology. Figure 1 shows powder X-ray diffraction patterns obtained from the products formed from reactions with 1.0:2:0 and 1.0:1.0 SiO_2:Mg_3N_2 molar ratios. Note that the $1.0SiO_2$:$2.0Mg_3N_2$ ratio produces a product with no silicon impurity. Each reacted pellet was ground and washed with 6.0 M HCl to remove unwanted byproducts. The isolated product is a fine powder that varies in color from brown (for a 1.0:1.0 ratio) to light gray (for a 1.0:2.0 ratio). Pure $MgSiN_2$ has a band gap of 4.8 eV,[25] and should be white. As the amount of Mg_3N_2 in the reaction mixture is increased above the 1.0:2.0 ratio, the product color changes to tan and then to brown with a concurrent reduction in crystallinity. Reactions with a 1.0:2.0 reagent ratio typically result in a 70% yield. Figure 2 shows SEM images of the fumed silica starting material and the washed $MgSiN_2$-containing product synthesized from a reaction with a 1.0:2.0 SiO_2:Mg_3N_2 molar ratio. EDS of this isolated product gave a Si:Mg molar ratio of 2:1 and an oxygen content of 15 wt %.

Silicon Source Variation. The silicon source was varied by substituting several other silicon-containing compounds for fumed silica in the reactant mixture. The results of these reactions are summarized in Table 1.

Rice hull ash, diatomaceous earth, and bottle glass are not pure SiO_2. However, they were treated as stoichiometric SiO_2 for the purpose of determining molar ratios. The composition

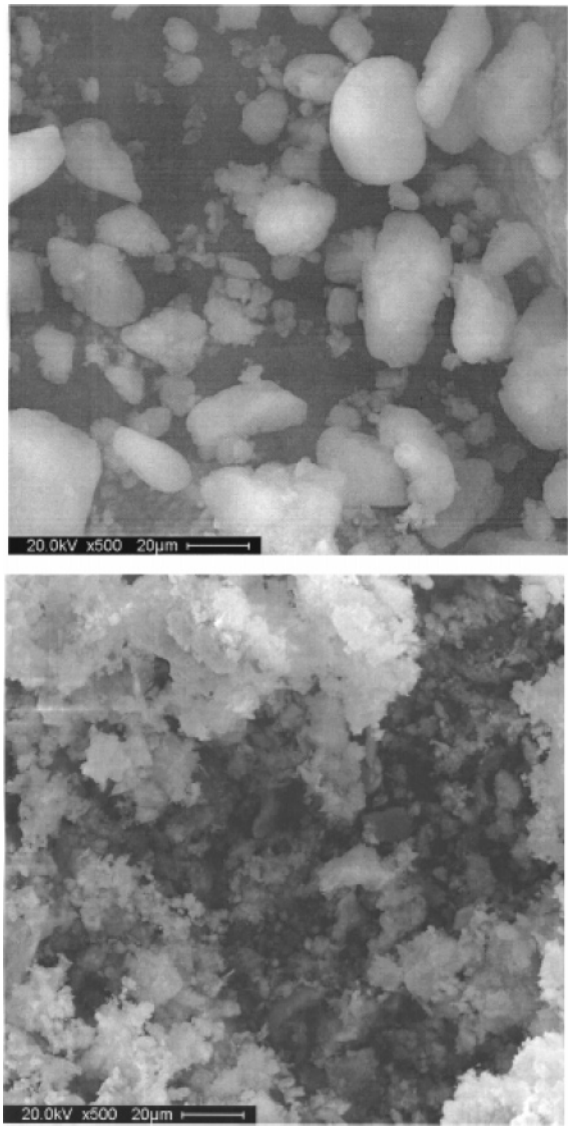

Figure 2. Scanning electron micrographs show the morphology of the reactant SiO_2, fumed silica (top), and the washed product $MgSiN_2$ (bottom) synthesized from a 1.0:2.0 molar ratio of SiO_2 to Mg_3N_2.

Table 1. Reactions Attempted To Synthesize $MgSiN_2$[a]

reaction	product
1.0 diatomaceous earth + $1.0Mg_3N_2$	Mg_2SiO_4 + Si
1.0 diatomaceous earth + $2.0Mg_3N_2$	$MgSiN_2${139} + Si
1.0 diatomaceous earth + $3.0Mg_3N_2$	$MgSiN_2${166} + Si
1.0 diatomaceous earth + $4.0Mg_3N_2$	$MgSiN_2${159} + Si
1.0 fumed silica + $2.0Mg_3N_2$	$MgSiN_2${169}
1.0 fumed silica + $2.0Mg_3N_2$ + $1.0NH_4Cl$	Mg_2SiO_4 + $MgSiN_2$ + Si
1.0 glass + $2.0Mg_3N_2$	$MgSiN_2${221} + Si trace
1.0 quartz + $2.0Mg_3N_2$	$MgSiN_2${257} + Si trace
1.0 quartz + $1.0Mg_3N_2$	Mg_2SiO_4 + Si
2.0 quartz + $1.0Mg_3N_2$	quartz + Mg_2SiO_4 + Si
1.0 rice hull ash + $2.0Mg_3N_2$	$MgSiN_2${158} + Si
1.0 rice hull ash + $1.0Mg_3N_2$	$MgSiN_2${199} + Si
2.0 rice hull ash + $1.0Mg_3N_2$	Mg_2SiO_4 + Si
1.0 sand + $2.0Mg_3N_2$	$MgSiN_2${122} + Si
$1.0SiO + 2.0Mg_3N_2$	$MgSiN_2${312} + Si

[a] For reactions that produce $MgSiN_2$, the intensity of the $MgSiN_2$(002) X-ray diffraction peak is given in braces.

(25) Groen, W. A.; Kraan, M. J.; de With, G. *J. Eur. Ceram. Soc.* **1993**, *12*, 413−420.

of diatomaceous earth can vary depending upon its source. Typically, it contains approximately 80 wt % silica, with the remaining weight consisting of TiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Na_2O, P_2O_5, and Mn_2O_3.[19,26] The approximate composition of rice hull ash is 94 wt % silica, with the remaining 6 wt % consisting of K_2O, CaO, MgO, MnO, Al_2O_3, and P_2O_5.[27−30]

Ground natural quartz produces a $MgSiN_2$ product that is more crystalline than that produced from fumed silica. The X-ray diffraction pattern of this product shows no evidence for crystalline quartz. Washed sea sand produces $MgSiN_2$ contaminated with significant amounts of quartz (SiO_2) and elemental Si. Reactions utilizing ground glass produced a tan product that does contain $MgSiN_2$, but it is contaminated with a significant amount of silicon, indicating an incomplete reaction. Diatomaceous earth and rice hull ash both produce $MgSiN_2$ of small crystallite size with significant Si contamination. The use of silicon monoxide, SiO, as a silicon source results in reactions that are explosively spontaneous. The product contains crystalline $MgSiN_2$ along with significant amounts of Si and SiO_2 contaminants.

Since an excess of Mg_3N_2 is required to produce a crystalline product free of silicon contamination (Figure 1), ammonium chloride (NH_4Cl) was added to the reaction mixture in an attempt to increase the local nitrogen content of the pellet during the reaction. However, ammonium chloride also serves to lower the reaction temperature.[12] The result of this reaction was a $MgSiN_2$ product of low crystallinity with Si contamination.

Initiation Conditions. The reaction initiation conditions were studied by performing reactions in both a microwave and evacuated quartz ampules heated to different temperatures. In a microwave oven, a pellet with a SiO_2:Mg_3N_2 ratio of 1.0:2.0 was heated until initiation occurred (approximately 2−3 min). The products from this reaction consisted of poorly crystalline $MgSiN_2$ and Si. A pellet with the same reactant ratio was placed in a quartz tube and heated to 1000 °C under dynamic vacuum for 12 h. The products of this reaction were Si and Mg_2SiO_4.

The effect of reaction temperature was explored by varying the type of initiation flame. Pellets with a SiO_2:Mg_3N_2 ratio of 1.0:2.0 were initiated with four different flames: 1100 °C (propane/air), 2500 °C (natural gas/oxygen), 2700 °C (hydrogen/oxygen), and 3300 °C (acetylene/oxygen).[31] All reactions produced $MgSiN_2$ as summarized in Table 2. The color of the product varied from brown at 1100 °C to gray at 3300 °C. The product color became increasingly more gray with higher initiation temperature. Lowering the reaction temperature results in a lower $MgSiN_2$ crystallinity (Table 2). The reaction initiated with a propane torch (1100 °C) produced the least crystalline $MgSiN_2$ and was the only product to contain detectable amounts of Si. The hydrogen/oxygen (2700 °C) initiated reaction produced the most crystalline $MgSiN_2$.

Table 2. Summary of $MgSiN_2$-Producing Reactions between Fumed Silica (SiO_2) and Mg_3N_2 Carried out at Different Temperatures[a]

flame type	temp (°C)	product	flame type	temp (°C)	product
propane	1100	$MgSiN_2${148} + Si	hydrogen/oxygen	2700	$MgSiN_2${231}
methane/oxygen	2500	$MgSiN_2${169}	acetylene/oxygen	3300	$MgSiN_2${177}

[a] The intensity of the $MgSiN_2$(002) X-ray diffraction peak is given in braces.

The real temperature of the reaction pellet will be lower than the maximum flame temperature reported in Table 2 due to thermal losses. The actual internal temperature of a reaction was monitored by embedding a K-type thermocouple inside the pellet. As a control experiment, the pellet was heated with a conventional Bunsen burner using natural gas (CH_4), which has a measured flame temperature of ∼1100 °C. The temperature at the inside of the reaction pellet reached a maximum of 970 °C after about 60 s.

By utilizing a furnace with SiC elements, a flame-free initiation temperature of 1450 °C can be achieved. The flame-initiated reaction that gave the most crystalline $MgSiN_2$ ($SiO_2 + 2Mg_3N_2$) was initiated under vacuum, nitrogen, and air. When this reaction was performed under vacuum at 1450 °C, a product consisting of mostly Si with a small amount of $MgSiN_2$ was obtained. The same reaction performed under nitrogen produced a product where the only crystalline phase present was $MgSiN_2$. Performing this reaction in air produced a product where the only phase present was $MgSiN_2$, but with a lower yield than the same reaction performed under nitrogen.

Thermal Analysis. Thermal events during the reaction were studied using differential thermal analysis. The reaction that produced the most crystalline $MgSiN_2$ free of other crystalline products ($SiO_2 + 2Mg_3N_2 \rightarrow MgSiN_2 + 2MgO + Mg_3N_2$) showed an exotherm around 1080 °C.

The presence of oxide impurities such as that produced by Mg−Si−O−N glass byproducts was gauged by heating the product to 1000 °C in a tantalum boat in a quartz tube held under dynamic vacuum for 12 h. Heating of the product from a reaction with a starting 1.0:1.0 reagent ratio of SiO_2 to Mg_3N_2 produced Mg_2SiO_4 as the only crystalline phase present by XRD. However, heating the product from the 1.0:2.0 reaction produced a minor amount of Mg_2SiO_4, while the majority of the sample remained unchanged. Oxide and silicon impurities are removed by washing the $MgSiN_2$ in molten $NaNH_2$. Figure 3 shows the change in the crystallinity of the $MgSiN_2$ product before and after washing. This wash dissolves 55% of the product, reducing the yield of a 1.0:2.0 reaction to 32%.

Thermogravimetric analysis was performed on the reaction that produced the best $MgSiN_2$ sample, as determined by XRD. This sample was the product of a reaction with a SiO_2:Mg_3N_2 ratio of 1.0:2.0. An initial water loss of 1.71% at 100 °C was followed by a weight gain of 10.78% between 800 and 1000 °C.

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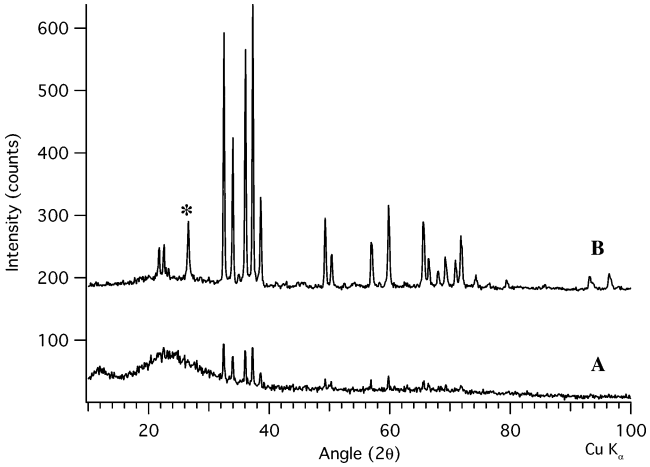

Figure 3. Powder X-ray diffraction patterns of $MgSiN_2$ before (A) and after (B) washing for 5 h in $NaNH_2$ at 275 °C. All peaks are from the $MgSiN_2$ product except the one marked with an asterisk, which is due to graphite (002) from the crucible.

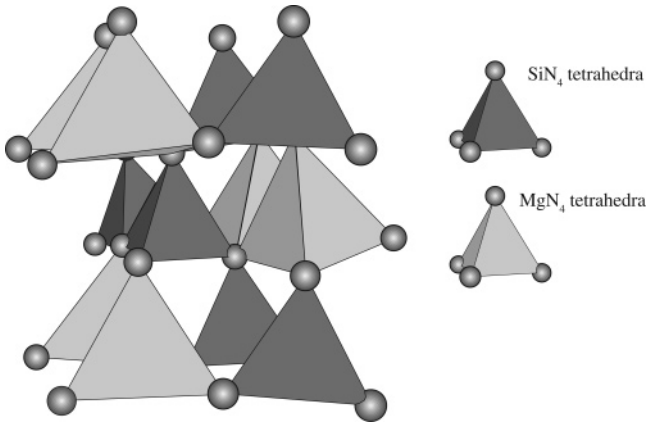

Figure 4. The structure of $MgSiN_2$ consists of alternating layers of infinite corner-sharing MgN_4 and SiN_4 tetrahedra.

Thermal Conductivity. Product from a reaction with a SiO_2:Mg_3N_2 ratio of 1.0:2.0 was hot pressed to produce a dark gray pellet with a thermal conductivity of 57 ± 10 W m^{-1} K^{-1} and a volume resistivity of $>6 \times 10^9$ Ω cm. EDS of this pellet gave a Si:Mg molar ratio of 2:1 and an oxygen content of 10%. The hardness of this material was comparable to that of silicon carbide.

Discussion

$MgSiN_2$ crystallizes in an orthorhombic unit cell, derived from the wurtzite (hexagonal ZnS) structure,[32] with lattice parameters of $a = 5.2790$ Å, $b = 6.4760$ Å, and $c = 4.9920$ Å. This structure, as shown in Figure 4, can be viewed as alternating layers of infinite corner-sharing tetrahedra of magnesium nitride (MgN_4) and silicon nitride (SiN_4). Small displacements of the tetrahedra reduce the symmetry to orthorhombic ($a \neq b \neq c$, all angles 90°).

The use of metathesis or double displacement reactions to synthesize $MgSiN_2$ offers a quick, energy-efficient route to its production. The mechanism by which this reaction goes to completion can be examined by looking at individual reactions that may occur during the heating of the reactant pellet. Elemental silicon can be produced by the reduction of SiO_2 when heated with Mg metal (eq 2).[33]

$$SiO_2 + 2Mg \rightarrow Si + 2MgO \quad (2)$$

This creates an amorphous form of silicon possessing a high surface area. The thermal decomposition of Mg_3N_2 at 800 °C, in the absence of O_2, produces Mg and N_2 as given in eq 3.[34]

$$Mg_3N_2 \rightarrow 3Mg + N_2 \quad (3)$$

Note that Mg_3N_2 is slowly converted to MgO and NH_3 upon exposure to humid air. This reaction is, however, slow enough to allow manipulation of the reagents in air without any significant degradation of the product quality. Additionally, the Mg_3N_2/SiO_2 reaction mixture is pressed into a pellet to minimize surface oxidation due to atmospheric air. The Mg_3N_2/SiO_2 mixture should, therefore, produce $MgSiN_2$ as given in eq 4. The net reaction results in the formation of MgO along with $MgSiN_2$ as given in eq 5.

$$Si + N_2 + Mg \rightarrow MgSiN_2 \quad (4)$$

$$SiO_2 + Mg_3N_2 \rightarrow MgSiN_2 + 2MgO \quad (5)$$

Reagent Ratios. The formation of $MgSiN_2$ from SiO_2 and Mg_3N_2 is an exothermic process. The enthalpy of reaction for eq 5 is −141.31 kJ/mol with a maximum theoretical adiabatic temperature of 2641 °C. This reaction is considerably more favorable than the formation of Si_3N_4 from the same reagents, as illustrated in eq 6.

$$3SiO_2 + 2Mg_3N_2 \rightarrow Si_3N_4 + 6MgO \quad (6)$$

This path has an enthalpy of reaction of −27.55 kJ/mol with a maximum theoretical adiabatic temperature of 268 °C. Although thermodynamically favorable, experimentally, a 1.0:1.0 ratio of SiO_2 to Mg_3N_2 does not produce phase-pure $MgSiN_2$. Figure 5 illustrates the relationship between the crystallinity of the $MgSiN_2$ product and Si impurities, if any, as detected by X-ray diffraction. Any Si detected in the product is likely due to local deficiencies of N_2 in the reaction zone. Another possibility is the formation of Mg_2SiO_4 (forsterite). This could occur in an oxygen-containing atmosphere since $MgSiN_2$ is unstable above 800 °C in air[25] and could react with either unreacted SiO_2 or the MgO byproduct as illustrated in eqs 7 and 8.

$$2SiO_2 + 2MgSiN_2 \rightarrow Mg_2SiO_4 + 3Si + 2N_2 \quad (7)$$

$$4MgO + MgSiN_2 \rightarrow Mg_2SiO_4 + Mg_3N_2 \quad (8)$$

Phase-pure $MgSiN_2$ can be produced by using an excess of Mg_3N_2. This allows for greater local N_2 content in the pellet and encourages complete reaction of Si produced as an intermediate. Controlled atmosphere studies indicate that the reaction should be initiated in a nitrogen-rich environ-

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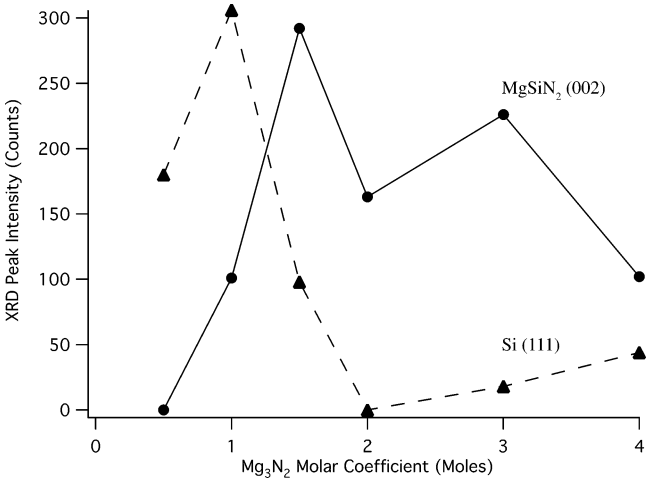

Figure 5. Powder X-ray diffraction peak intensities for reactions of the type $SiO_2 + nMg_3N_2$. The intensity of the $MgSiN_2$(002) peak is plotted along with the intensity of the Si(111) peak. The reaction with a molar ratio of $1.0SiO_2$:$2.0Mg_3N_2$ produced X-ray-pure $MgSiN_2$. A reactant ratio of 1.0:0.5 produced only Si.

ment. The excess Mg_3N_2 required for reactions performed in air may be required to reduce the local oxygen content surrounding the reaction pellet. Thermogravimetric analysis of the product from a reaction with a SiO_2:Mg_3N_2 ratio of 1.0:2.0 indicates that oxidation starts occurring at 800 °C. This is consistent with previous studies of $MgSiN_2$.[25] Analysis of the product after heating in air to 1000 °C indicates that the major crystalline phase present is Mg_2SiO_4. However, the compound only experienced a mass gain of 10.78%, whereas pure $MgSiN_2$ should show a mass gain of 24% if it is entirely converted to Mg_2SiO_4 and SiO_2. The lower value may be due to the formation of other amorphous compounds in the Mg−Si−N−O system or the presence of oxide impurities in the $MgSiN_2$ product itself. These byproducts can be removed by washing the material in a sodium amide melt.

Silicon Source Variation. The use of different silicon sources was carried out to ascertain if the dynamics of the reaction could be changed to enhance the crystallinity of the $MgSiN_2$ product. The mineral SiO_2 (quartz), when ground to a powder, produces the most crystalline $MgSiN_2$. However, fumed silica, a very pure form of SiO_2, produces less crystalline $MgSiN_2$. Hence, the purity of the starting Si-containing reagent does not appear to be a critical factor affecting the synthesis of highly crystalline $MgSiN_2$. Particle size, on the other hand, does appear to play an important role in the synthesis of crystalline $MgSiN_2$. A larger particle size can lead to severe inhomogeneities in the reaction pellet. This can be seen with reactions involving sea sand where the particle size is on the order of 0.5−1.0 mm. The large grain size of the reactant leads to an incomplete reaction. The product is contaminated with significant amounts of quartz (SiO_2) and Si. In contrast, fumed silica can be considered to be essentially nanoparticles of SiO_2. However, it forms clumps (see Figure 2a) that can trap gases and may lead to a product that contains a significant amount of glassy impurities. This implies that there is an ideal particle size for $MgSiN_2$ formation somewhere between the two size regimes represented by fumed silica (nanoparticles) and sea sand (0.5−1.0 mm).

It is interesting to note that ground bottle glass, diatomaceous earth, and rice hull ash each produce $MgSiN_2$ when reacted with Mg_3N_2. This suggests that $MgSiN_2$ can be produced from a variety of SiO_2 sources. In each of these cases, the product is contaminated with Si and hence the purity of the starting material is an important factor in $MgSiN_2$ production. This is understandable since ground bottle glass is actually a solution of SiO_2, CaO, Na_2O, and other oxides rather than pure silica. Therefore, its silicon content will actually be lower than expected. Optimization of reactions involving these alternative SiO_2 sources could provide an inexpensive source of Si for the production of $MgSiN_2$ especially if high purity is not required.

The mechanism of formation of $MgSiN_2$ may be through the formation of Si_3N_4. Silicon nitride can be formed by the reaction of hot Si with N_2 gas.[35] The conditions inside a reaction pellet can approximate these conditions. Alkali-metal and alkaline-earth-metal nitrides are known to react with silicon nitride to form mixed-metal nitrides as given in eq 9.[32,34,36]

$$Si_3N_4 + Mg_3N_2 \rightarrow 3MgSiN_2 \qquad (9)$$

However, silicon nitride was never detected in products formed from these reactions. Yet, this may simply be due to the greater thermodynamic driving force to form $MgSiN_2$ (−141.31 kJ/mol) over Si_3N_4 (−27.55 kJ/mol).

The addition of NH_4Cl to the reaction pellet serves as both a source of NH_3 and a heat sink.[12] The result is a lower temperature in the reacting pellet. The product from reactions with NH_4Cl had low crystallinity and a large amount of Si contamination. This suggests that higher temperatures are required to ensure complete nitridation of the Si in the reaction pellet.

Initiation Conditions. The effect of temperature on the quality of the product was further tested by varying the initiation flame. Since these reactions do not self-propagate, the flame was kept on each pellet for 20 s to ensure uniform reactions. By varying the flame type, the reaction temperature can be changed from 1100 to 3300 °C. It was found that the lowest temperature flame produced a poorly crystalline product contaminated with Si. This is in agreement with the data obtained from the reaction containing NH_4Cl. Higher temperature flames (≥2500 °C) all produced crystalline $MgSiN_2$ with no Si impurities detectable by XRD. It is interesting to note that the H_2/O_2 flame (2700 °C) produces the most crystalline product.

The reaction duration was examined by varying the initiation methods. Microwave initiation results in very fast reactions that cool quickly to ambient temperature. Microwave-initiated reactions produced poorly crystalline $MgSiN_2$ and Si due to the high reaction speed. In these rapid reactions, the pellet did not achieve a temperature high enough to ensure complete reaction nor did the pellet remain long

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enough at a sufficiently high temperature to allow an increase in the crystallinity of the product by Ostwald ripening of the as-formed $MgSiN_2$. Reactions carried out in quartz ampules under dynamic vacuum at 1000 °C for 12 h only produced Mg_2SiO_4. This indicates that Mg_2SiO_4 is the thermodynamically favored phase and that it readily forms in the presence of unreacted SiO_2 and the byproduct MgO. This gives further support to the argument that flame-initiated reactions are kinetically controlled.

With a band gap of 4.8 eV,[25] pure $MgSiN_2$ should be white. The color of many of the products suggests that other amorphous phases are present in the powders produced. It should be noted that the reaction that gave the least amount of Si impurity also produced a product with a color closest to the gray reported in the literature.[25]

Purification. A major dilemma in the formation of $MgSiN_2$ from silica is the subsequent formation of unwanted Mg−Si−N−O glasses.[37−39] The presence of these glasses can be inferred by a large broad structure around $2\theta = 20°$ in the powder diffraction patterns of the products of these reactions. It is fortunate that $MgSiN_2$ exhibits limited solubility in these glasses. The glass formed can be removed with concentrated nitric acid to which $MgSiN_2$ is resistant. By varying the reactant ratio and adding an additional 12 h wash with concentrated HNO_3, the amount of amorphous glass in the product can be essentially eliminated.

An alternative method to remove impurities involves the use of molten $NaNH_2$. Molten $NaNH_2$ is known to attack glass, silica, and even silicon.[40] The removal of amorphous materials from the $MgSiN_2$ product indicates that $NaNH_2$ attacks unwanted byproducts faster than the desired $MgSiN_2$ product. The loss of 55% of the starting product suggests that a significant amount of amorphous material is present in the reaction product. The use of $NaNH_2$ may also allow the removal of Si from reactions involving alternative silica sources.

Thermal Analysis. The initiation of the $MgSiN_2$-forming reaction (eq 5) is evidenced by an exotherm at 1095 °C, which is consistent with the boiling point of Mg (1090 °C). It has been found that solid-state metathesis reactions are generally initiated upon a phase change in one of the reagents.[41] In this case, Mg_3N_2 begins to decompose to elemental Mg to initiate the reaction. The long heating times required to ensure complete reactions may be due to the need to fully decompose Mg_3N_2.

For optimal thermal characteristics, it is desirable to produce $MgSiN_2$ free of oxide impurities. When $MgSiN_2$ is heated in the presence of MgO and SiO_2, it slowly converts to Mg_2SiO_4.[42] A qualitative measure of the oxide content of the most crystalline product was ascertained by heating in vacuo at 1000 °C for an extended period of time. It was found that the product contained only a small amount of Mg_2SiO_4. In contrast, a less crystalline product produced with a nonoptimal amount of Mg_3N_2 gave a powder that, after heating, consisted entirely of Mg_2SiO_4.

Thermal Conductivity. The dramatic decrease in the agglomerate size from fumed silica (micrometer) to synthesized $MgSiN_2$ (submicrometer) results in a product that should be easily compacted. This material was hot pressed into a pellet that was 98% dense. The dense billet exhibited a thermal conductivity of 57 ± 10 W m^{-1} K^{-1}. This is greater than previously measured values which ranged from 17 to 38 W m^{-1} K^{-1}.[1] However, this is still less than the theoretical maximum value of 75 W m^{-1} K^{-1} and within the range of a suggested maximum thermal conductivity of 50 W m^{-1} K^{-1}.[1] X-ray diffraction analysis of the sintered pellet indicates that the only crystalline phases present are α-Si_3N_4 and $MgSiN_2$. The Si:Mg mole ratio of 2:1 obtained by EDS indicates that the pellet does not consist of pure $MgSiN_2$. With a thermal conductivity of 30 W m^{-1} K^{-1}, the presence of Si_3N_4 impurities does not account for the high thermal conductivity measured. This high thermal conductivity may be due to the presence of amorphous SiC (120 W m^{-1} K^{-1}) or Si (141 W m^{-1} K^{-1}). Neither was detected by XRD, and the high volume resistivity ($>6 \times 10^9$ Ω cm) suggests that these phases may not be present in high concentrations. The qualitative observation of the hardness of this material indicates that its hardness is on the order of silicon carbide. This implies that Si_3N_4 and Si (both of which are softer than SiC) are not major impurities.

Conclusions

$MgSiN_2$ can be synthesized from inexpensive sources of silica by reaction with Mg_3N_2. The general equation is $SiO_2 + nMg_3N_2 \rightarrow MgSiN_2 + 2MgO +$ glass. The quality of the $MgSiN_2$ produced is directly related to the amount of Mg_3N_2 utilized in the reaction and the temperature of the initiating flame. With 2 mol of Mg_3N_2, the most crystalline, X-ray-pure $MgSiN_2$ was produced. Impurities and amorphous byproducts can be effectively removed by using a molten sodium amide ($NaNH_2$) bath. The speed with which these reactions go to completion potentially offers an attractive route to the production of large quantities of $MgSiN_2$. Future research in controlling the composition of the amorphous glass byproduct could result in an even more crystalline product and facilitate removal of any byproduct glasses.

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