

# Dibromoborane-Dimethyl Sulfide: A Simple Molecular Precursor for the Formation of Bulk Powders and Fiber Coatings of Boron Nitride

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The Lewis base-borane adduct  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2$  has been found to be an effective molecular precursor for the formation of high-purity bulk powders and ceramic fiber coatings of boron nitride. Bulk pyrolyses of  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2$  under ammonia carried out at various temperatures between 650 and 1500 °C resulted in the formation of BN powders, as characterized by diffuse-reflectance IR and X-ray diffraction spectra, density measurements, and elemental analysis. Thermogravimetric analysis studies in air demonstrated that BN powders prepared at temperatures as low as 650 °C exhibit oxidative stability to 820 °C. Materials of increased purity, crystallinity, and oxidative stability were prepared at higher temperatures. Boron nitride fiber coatings were achieved on  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  and SiC fibers by dip coating either single fibers or fiber bundles in 2-18% (w/w) solutions of  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2$  followed by pyrolysis of the coated fibers under an ammonia atmosphere to a maximum temperature of 1000 °C. Scanning electron microscopy and Auger electron spectroscopy studies confirmed the formation of BN coatings.

## Introduction

Interest in the development of ceramic composite materials stems from a desire to improve structural integrity over that of a single ceramic component.<sup>1</sup> For example, ceramic fiber reinforced composites are known to exhibit increased strength and toughness due to a reduction in crack propagation.<sup>1,2</sup> A suitable ceramic fiber coating can further enhance the strength of a ceramic fiber composite by increasing toughness by decreasing the interfacial shear strength between the fiber and matrix and thus increase the potential for fiber pullout.<sup>2</sup> In addition, the fiber coating may also serve as a diffusion barrier between the fiber and matrix materials and thus inhibit chemical reactions between these materials at high temperatures.<sup>1-3</sup> Because of its excellent specific strength, chemical resistance, and lubricating properties, boron nitride is an attractive prospect as a coating for fibers in ceramic fiber reinforced composites.<sup>3</sup>

Previous methods for the formation of coatings or thin films of boron nitride have generally relied on the use of chemical vapor deposition (CVD) techniques, employing mixtures of  $\text{NH}_3$  and volatile borane species such as  $\text{BCl}_3$ ,  $\text{B}_2\text{H}_6$ , and  $\text{B}_3\text{N}_3\text{H}_6$ .<sup>4</sup> For example, conventional CVD techniques are used for the preparation of thin films of BN from a  $\text{BCl}_3\text{-NH}_3\text{-H}_2$  mixture at 1000-1400 °C, while plasma-assisted CVD of a  $\text{B}_2\text{H}_6\text{-NH}_3\text{-H}_2$  mixture results in a deposition of a thin layer of BN in the temperature range 400-700 °C.<sup>4</sup> Although the CVD technique offers an effective pathway for depositing a uniform layer of a ceramic on a variety of substrates, these procedures are often time consuming and costly and require specialized equipment.

An alternative method for generating BN coatings could employ a nonvolatile chemical precursor<sup>5</sup> that could be precoated on the desired substrate and then be thermally decomposed to form a boron nitride layer. With this goal in mind, several boron-based polymer<sup>6-10</sup> systems have been developed as potential precursors to BN coatings, although such applications have not yet been reported. Simple molecular precursors to boron nitride should also

be possible. We report herein that the Lewis base-borane adduct  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2$  is an excellent precursor for the

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formation of both bulk powders and ceramic fiber coatings of boron nitride.

### Experimental Section

All manipulations were performed using standard high-vacuum or inert-atmosphere techniques as described by Shriver.<sup>11</sup> Fiber coatings were performed in glovebags purged with argon.

**Materials.** Ammonia was purchased from Matheson and used as received. Dibromoborane-dimethyl sulfide complex was purchased from Aldrich, either neat or as a 1.0 M solution in dichloromethane. The fibers, Du Pont PRD-166 ( $\text{Al}_2\text{O}_3/\text{ZrO}_2$ ) and Nicalon (SiC) were obtained from Dr. John Bolt of the Fibers Department at Du Pont and pretreated by heating to 600 °C in air.

**Physical Measurements and Instrumentation.** Diffuse-reflectance infrared spectra were obtained on a Perkin-Elmer 7770 Fourier transform spectrophotometer with the appropriate diffuse-reflectance attachment. Thermogravimetric analyses (TGA) were performed on either on Du Pont 990 or 2100 thermal analyzer with a 951 TGA. X-ray powder diffraction (XRD) spectra were obtained on a Rigaku Geigerflex X-ray powder diffractometer. Scanning electron microscopy (SEM) was performed on either Phillips 500 or 500X scanning electron microscopes. Auger electron spectra (AES) were obtained on a Perkin-Elmer Phi 600 scanning Auger microprobe operating at 3-kV primary voltage with a beam current of 0.1  $\mu\text{A}$ , yielding a spot size of  $\sim 0.5 \mu\text{m}$ .  $\text{Ar}^+$  ion sputtering was performed using a differentially pumped ion gun operating at 3 kV with a beam current of 1  $\mu\text{A}$ , yielding a spot size of 1 mm. The ion sputtering rate was 125  $\text{\AA}/\text{min}$  as measured on a 1000- $\text{\AA}$  film of silicon dioxide on silicon. It was assumed that the sputtering rate of BN was similar. The base pressure of the system was  $5 \times 10^{-10}$  Torr. During ion sputtering the pressure increased to  $3 \times 10^{-8}$  Torr. Densities were measured by flotation using mixtures of dibromomethane, dichloromethane, and dibromomethane. Elemental analyses were performed at Galbraith Laboratories.

**Bulk Pyrolysis of  $(\text{CH}_3)_2\text{S-BHBr}_2$  to 1350 °C.** Into a boron nitride boat under argon was syringed 2.62 g of  $(\text{CH}_3)_2\text{S-BHBr}_2$ . The boat was placed in a quartz tube that was immediately transferred to a tube furnace. After exposure of the sample to  $\text{NH}_3$  at room temperature for 5 min, the furnace temperature was increased at a rate of 10 °C/min to a maximum temperature of 1250 °C and held at this temperature for 6 h. The sample was then cooled under argon to room temperature. The resulting material was white with a slight pinkish tinge and weighed 0.26 g. The sample was then ground with a mortar and pestle, placed in a boron nitride boat in a mullite tube, and heated under  $\text{NH}_3$  to a maximum temperature of 1350 °C for 3 h and maintained at this temperature under argon for an additional 6 h. After cooling under argon, the material was pure white in appearance and weighed 0.249 g, corresponding to a chemical yield of 89.5% and a ceramic yield of 9.5% (theoretical 10.6%). Anal. Calcd for BN: B, 43.55; N, 56.45. Found: B, 44.40; N, 53.43, C, 0.18; H, 0.17; S, 0.032. The X-ray powder diffraction data indicated the presence of turbostratic<sup>12</sup> BN, and the diffuse-reflectance IR spectrum was consistent with that previously reported for BN.<sup>13</sup> The density of the material was 1.90 g/mL.

The conversion of  $(\text{CH}_3)_2\text{S-BHBr}_2$  to BN under an  $\text{NH}_3$  atmosphere was also monitored by TGA. In this experiment 0.036 g of  $(\text{CH}_3)_2\text{S-BHBr}_2$  was placed in a platinum boat and heated at 20 °C/min in the TGA apparatus under 100  $\text{cm}^3/\text{min}$  of 80%  $\text{NH}_3/\text{Ar}$  until a final temperature of 1100 °C was reached. After

cooling, 0.0038 g of a white material was obtained, corresponding to a ceramic yield of 10.55%.

**Bulk Pyrolysis of  $(\text{CH}_3)_2\text{S-BHBr}_2$  to 250 °C.** In an experiment similar to that described above, 1.82 g of  $(\text{CH}_3)_2\text{S-BHBr}_2$  was pyrolyzed under ammonia at a rate of 10 °C/min to a maximum temperature of 250 °C and held at this temperature for 1 h. The sample was then cooled under argon to room temperature. The resulting material was white with a slight orange tinge and weighed 1.26 g, corresponding to a weight loss of 30.8%. Anal. Found: B, 5.25; N, 17.42; C, 0.10; H, 3.75; S 0.12; Br, 70.27. IR (Diffuse) 3435 (w), 3140 (s), 3035 (s), 2805 (m), 2365 (w), 1960 (m), 1720 (m), 1510 (m), 1400 (s), 1115 (w), 780 (m), 690 (m), 600 (m)  $\text{cm}^{-1}$ .

The reaction of  $(\text{CH}_3)_2\text{S-BHBr}_2$  with gaseous  $\text{NH}_3$  to a maximum temperature of 255 °C was also carried out in the TGA. In this experiment 0.094 g of  $(\text{CH}_3)_2\text{S-BHBr}_2$  was placed in a platinum boat and heated at 10 °C/min in the TGA under 100  $\text{cm}^3/\text{min}$  of 80%  $\text{NH}_3/\text{Ar}$  until a final temperature of 255 °C was reached. After cooling under  $\text{NH}_3$ , the resulting white material weighed 0.060 g, corresponding to a weight loss of 36.2%. Anal. Found: B, 5.49; N, 16.08; C, 0.32; H, 3.82; S, 0.14; Br, 68.75. IR (diffuse) 3435 (w), 3130 (s), 3035 (s), 2800 (m), 2514 (m), 2365 (w), 2344 (w), 1955 (w), 1720 (m), 1400 (s), 1130 (m), 910 (m), 775 (m), 710 (m)  $\text{cm}^{-1}$ .

**Bulk Pyrolyses to 650 °C and Above.** The reaction of  $(\text{CH}_3)_2\text{S-BHBr}_2$  with gaseous  $\text{NH}_3$  was carried out in stages at or above 650 °C. A 2.05-g sample of  $(\text{CH}_3)_2\text{S-BHBr}_2$  was heated in a mullite tube under  $\text{NH}_3$  first to 650 °C for 12 h and then subsequently to 1000 (14 h), 1200 (14 h) and 1500 °C (14 h). At each stage, a sample of the solid was removed from the pyrolysis boat and examined by IR and XRD. The density of each material was also measured, and its oxidative stability examined by TGA under air in the temperature range 25–1100 °C.

In a separate series of experiments, individual samples of  $(\text{CH}_3)_2\text{S-BHBr}_2$  were pyrolyzed under ammonia for extended periods ( $\sim 60$  h) at 650 (5.79 g), 1000 (5.39 g), 1200 (6.36 g) and 1500 °C (5.29 g). The resulting ceramic powders, 0.53 g (9.2% ceramic yield), 0.47 g (8.7%), 0.58 g (9.1%), 0.49 (9.3%), respectively, were examined by IR, XRD, and elemental analysis and their oxidative stabilities examined as described above. Anal. Calcd for BN: B, 43.55; N, 56.45. Found: (650 °C sample) B, 37.96; N, 50.99; C, 0.50; H, 1.16; Br, 0.10; S, <0.05; (1000 °C sample) B, 39.49; N, 58.68; C, 0.39; H, 0.48; S, <0.005; Br, 0.004; (1200 °C sample) B, 43.46; N, 55.60; C, 0.28; H, 0.19; S, 0.025; Br, 0.094.

**Fiber Coatings.** Alumina ( $\text{Al}_2\text{O}_3$ )/ $\text{ZrO}_2$  or Nicalon (SiC) fibers were coated by dipping individual fibers into a 1 M (18%) solution of  $(\text{CH}_3)_2\text{S-BHBr}_2$  in  $\text{CH}_2\text{Cl}_2$  under nitrogen. The fibers were then placed in a boron nitride boat that was subsequently transferred to a tube furnace. A slow ammonia flow was then passed over the fibers for 5–10 min. The furnace temperature was then increased at a rate of 10 °C/min to a maximum temperature of 1000 °C. The fibers were subsequently cooled to room temperature under an argon flow. The resulting coated fibers were examined by both SEM and AES. Fiber bundles were dip-coated in diluted solutions of  $(\text{CH}_3)_2\text{S-BHBr}_2$  in  $\text{CH}_2\text{Cl}_2$  (PRD-166 (7% w/w), SiC (2–7% w/w)). The precoated fiber bundles were then transferred to a tube furnace and treated with  $\text{NH}_3$  under a temperature regime similar to that described above.

### Results and Discussion

A molecular precursor route may offer a number of advantages over vapor deposition methods for the production of ceramic materials, including greater control of stoichiometry, ceramic formation at lower temperatures, and higher processibility.<sup>5</sup> Perhaps the simplest molecular species containing boron and nitrogen that might be considered as a potential precursor to BN is the Lewis base-borane  $\text{NH}_3\text{-BH}_3$ . The decomposition reactions of  $\text{NH}_3\text{-BH}_3$  have, in fact, been previously studied by Geanangel, who examined reactions of  $\text{NH}_3\text{-BH}_3$  both in solution and in the solid state. In solution, in aprotic solvents, the compound is found to decompose above 80 °C to various species including cyclotriborazane and borazine, as well

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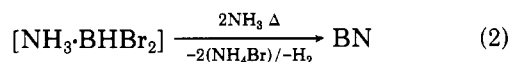
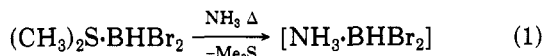
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as oligomeric  $(\text{BNH})_x$  materials.<sup>14</sup> This result is consistent with earlier observations that upon standing, solutions of  $\text{NH}_3\cdot\text{BH}_3$  deposit an insoluble material  $[\text{BH}_2(\text{NH}_3)_2]^+\text{BH}_4^-$ ,<sup>15</sup> a known precursor of BN cyclics.<sup>15,16</sup> Thermal decomposition of  $\text{NH}_3\cdot\text{BH}_3$  in the solid state leads to a variety of products depending on the conditions employed. Heating the compound above its melting point (115–116 °C) results in partial sublimation and some decomposition leading to the formation of  $\text{B}_2\text{H}_6$ ,  $\text{B}_3\text{N}_3\text{H}_6$ , and  $(\text{BNH})_x$  polymeric materials.<sup>17</sup> High-temperature pyrolysis (950 °C) of  $\text{NH}_3\cdot\text{BH}_3$  in a platinum-covered glassy carbon crucible has been reported to result in a 65% ceramic yield of BN.<sup>10</sup>

Despite the fact that bulk pyrolysis of  $\text{NH}_3\cdot\text{BH}_3$  leads to the formation of BN powder, the applications of this material as a chemical precursor for the generation of BN coatings appear limited. Indeed, plasma-assisted CVD of  $\text{NH}_3\cdot\text{BH}_3$ , even at high energy, produces a material with high hydrogen content,  $\text{BNH}_{0.5}$ .<sup>18</sup> Among the inherent drawbacks in the use of  $\text{NH}_3\cdot\text{BH}_3$  for coating or film formation are its low solubility and stability in most solvent systems and its volatility under mild thermal conditions.

We have now found the Lewis base-borane complex  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2$  to be a highly effective precursor for the production of bulk powders and coatings of boron nitride which circumvents many of the problems associated with the use of  $\text{NH}_3\cdot\text{BH}_3$  as a precursor. It is commercially available or easily synthesized by bromination of  $(\text{CH}_3)_2\text{S}\cdot\text{BH}_3$ ,<sup>19</sup> highly soluble in a variety of polar and nonpolar solvents, and has low volatility. Key features of  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2$  as a precursor are that the adduct is thermally stable at ambient temperatures, allowing the formation of films and coatings, but is chemically reactive with ammonia, resulting in complete displacement of the  $(\text{CH}_3)_2\text{S}$  base under mild conditions.<sup>20</sup> The resulting ammonia adduct is highly unstable with respect to hydrogen-halide loss<sup>21</sup> and can decompose cleanly to boron nitride, as suggested in eq 1 and 2.



**Bulk Conversion Reactions.** The bulk ceramic conversion reaction of  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2$  was initially studied by pyrolysis of the neat liquid under a flow of pure  $\text{NH}_3$  gas, at a heating rate of 10 °C/min in the temperature range

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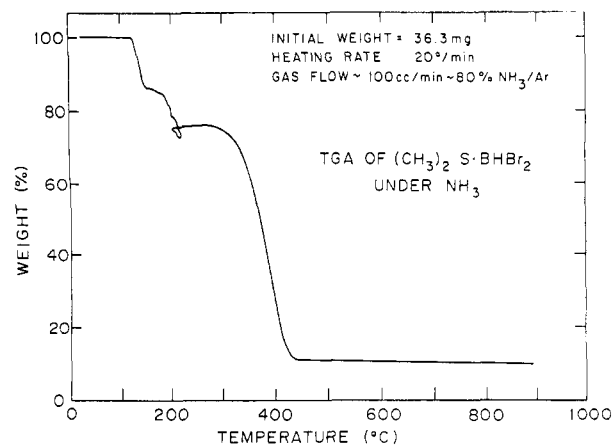
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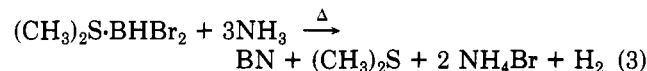
**Figure 1.** TGA of  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2$  under  $\text{NH}_3$ . (The loop observed near 200 °C is characteristic of a rapid exothermic reaction resulting in temporary overheating of the thermocouple adjacent to the sample.)

**Table I.** Ceramic Conversion Reactions

pyr temp, °C	reaction time, h	density, g/mL	$d(002)$ , Å	emp formula
650	12	1.68	3.67	$\text{B}_{1.0}\text{N}_{1.04}\text{C}_{0.04}\text{H}_{0.32}$
	60	1.71	3.65	
1000	14	1.91	3.60	$\text{B}_{1.0}\text{N}_{1.15}\text{C}_{0.009}\text{H}_{0.13}$
	60	1.93	3.57	
1200	14	1.91	3.53	$\text{B}_{1.0}\text{N}_{0.99}\text{C}_{0.006}\text{H}_{0.05}$
	60	1.93	3.45	
1350 <sup>a</sup>	9	1.90	3.44	$\text{B}_{1.0}\text{N}_{0.93}\text{C}_{0.004}\text{H}_{0.04}$
1500	14	2.00	3.45	
	60	2.18	3.45	

<sup>a</sup> Sample also treated at 1250 °C for 6 h.

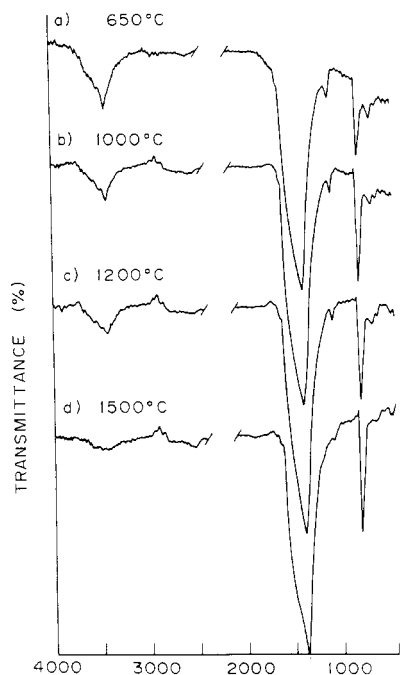
25–1350 °C. A pure white material was produced in 9.5% ceramic yield and 89.5% chemical yield, based on eq 3.



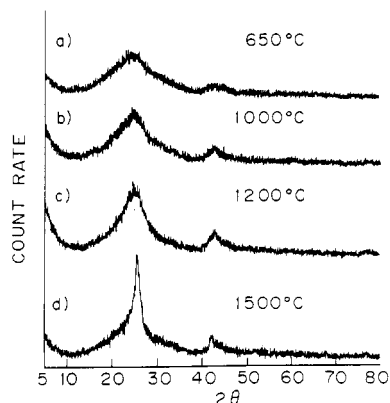
Elemental analysis of the ceramic indicated an empirical formula  $\text{B}_{1.0}\text{N}_{0.93}$ , with only low levels of carbon 0.18%, hydrogen 0.17%, and sulfur 0.032% impurities. The diffuse reflectance infrared spectrum was consistent with those previously reported for boron nitride<sup>13</sup> containing a broad BN stretching band over the frequency range 1556–1390  $\text{cm}^{-1}$  along with a strong absorption at 794  $\text{cm}^{-1}$ , which has been assigned to a B–N–B bending vibration. The spectrum contained no bands in the 3400- $\text{cm}^{-1}$  region, indicating no N–H impurities in this material. The material also exhibited an X-ray powder diffraction pattern characteristic of turbostratic BN,<sup>12</sup> thus indicating that while the boron nitride layer structure had been formed, the layers still had random rotational and translational order.

The conversion of  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2$  under  $\text{NH}_3$  was also studied by thermogravimetric analysis, as shown in Figure 1. A weight loss of ~25% occurred between 25 and 200 °C, suggesting an initial displacement of  $(\text{CH}_3)_2\text{S}$  by  $\text{NH}_3$  from the  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2$  complex. No further changes were observed until 270 °C. At this temperature a large rapid weight loss was observed ending at 450 °C. The final weight loss was 89.4% corresponding to a ceramic yield of 10.6%. Thus, the TGA study of the conversion of  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2$  to BN is consistent with the bulk pyrolysis reactions and supports the process shown above in eq 1.

To determine whether  $(\text{CH}_3)_2\text{S}$  was completely replaced by  $\text{NH}_3$  as a preliminary step in the conversion process, bulk and TGA pyrolyses were carried out to a maximum temperature of 255 °C, and the products isolated. Ele-



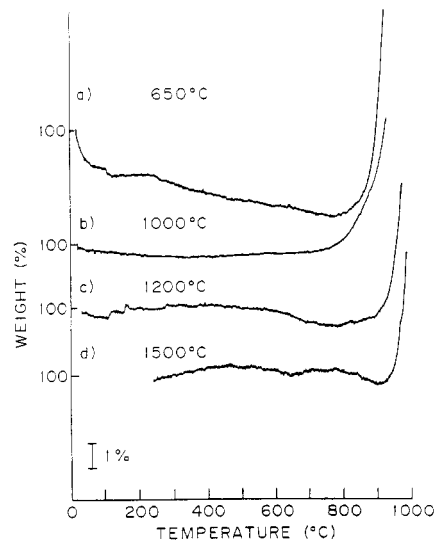
**Figure 2.** Diffuse-reflectance infrared spectra of BN powders prepared from pyrolysis of  $(\text{CH}_3)_2\text{S-BHBr}_2$  under  $\text{NH}_3$  at (a) 650 °C/12 h, (b) 1000 °C/14 h, (c) 1200 °C/14 h, (d) 1500 °C/14 h. Absorptions due to residual atmospheric  $\text{CO}_2$  near 2300  $\text{cm}^{-1}$  are removed.



**Figure 3.** X-ray powder diffraction spectra of BN powders prepared from pyrolysis of  $(\text{CH}_3)_2\text{S-BHBr}_2$  under  $\text{NH}_3$  at (a) 650 °C/12 h, (b) 1000 °C/14 h, (c) 1200 °C/14 h, (d) 1500 °C/14 h.

mental analyses of these materials (S, 0.12% and 0.14%) confirmed that  $(\text{CH}_3)_2\text{S}$  was essentially quantitatively displaced by 255 °C. Diffuse-reflectance IR spectra of these materials also showed the presence of  $\text{NH}_4\text{Br}$ , indicating that any intermediate ammonia-dibromoborane complex formed in the reaction has also decomposed by this temperature.

Since the TGA results indicated that the major weight loss was complete by 600 °C, a range of bulk pyrolyses under  $\text{NH}_3$  were performed on a single sample of  $(\text{C-H}_3)_2\text{S-BHBr}_2$  above 600 °C (650, 1000, 1200, 1500 °C) to compare the chemical and physical properties of BN prepared at these temperatures. After pyrolysis at each of the above temperatures for a period of 12–14 h, a sample of powder was removed from the pyrolysis boat, and the diffuse-reflectance IR (Figure 2), XRD (Figure 3), oxidative stability (Figure 4), and density (Table I) recorded. The diffuse-reflectance IR spectra of the samples prepared at lower temperatures showed the presence of NH species, as evidenced by the NH stretch at 3435  $\text{cm}^{-1}$ , which progressively decreased (Figures 2b–d) upon treatment of the



**Figure 4.** TGA under air of BN powders prepared from pyrolysis of  $(\text{CH}_3)_2\text{S-BHBr}_2$  under  $\text{NH}_3$  at (a) 650 °C/12 h, (b) 1000 °C/14 h, (c) 1200 °C/14 h, (d) 1500 °C/14 h.

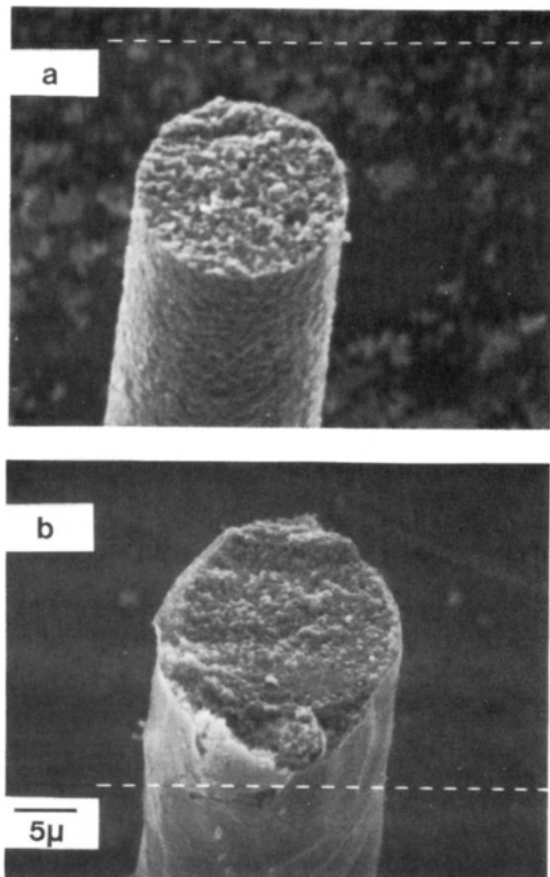
sample at higher temperatures. The XRD measurements indicate that even at 650 °C turbostratic BN is present and that at higher temperatures gradual organization of the lattice occurs, as evidenced by the sharpening of the 002 peak and its shift toward the 3.33-Å value observed for hexagonal boron nitride.<sup>22</sup> Likewise, the density measurements indicate a progressive densification of the materials at higher temperatures. Materials obtained at 1500 °C approach the reported densities of 2.2–2.4 g/mL for h-BN.<sup>22</sup>

To determine the effect of pyrolysis time on the properties of the BN powders, pyrolyses on individual samples were carried out for ~60 h at 650, 1000, 1200, and 1500 °C. Consistent with the IR studies discussed above, the elemental analyses of materials prepared at lower temperatures indicated higher hydrogen contents which decreased at higher pyrolysis temperatures: 650 (1.16%), 1000, (0.48%), 1200 °C (0.19%). Likewise the diffuse-reflectance IR spectra of the lower temperature 60-h samples showed NH stretching absorptions, although of lower intensities than those obtained in the comparable 12–14-h reactions. Given the NH stretch observed in the IR of these materials and the fact that their elemental analyses showed only low levels of Br at 650 (0.10%), 1000 (0.004%), and 1200 °C (0.094%), the hydrogen impurities are most probably due to incomplete removal of NH species in forming the BN framework rather than residual  $\text{NH}_4\text{Br}$ . The XRD data (Table I) for the 60-h pyrolyses also exhibit a slight increase in crystallinity as evidenced by the shift in the 002 peak to lower values.

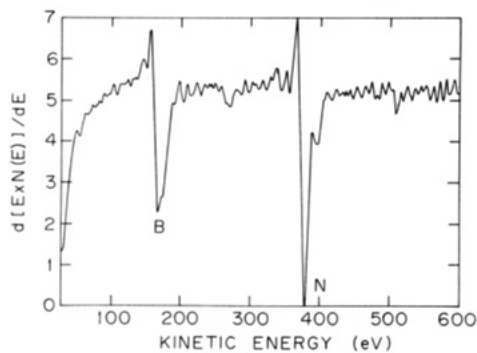
One of the most important properties of BN is its oxidative resistance. The oxidative stabilities of the boron nitride samples prepared at different temperatures were evaluated by TGA under air, as shown in Figure 4. The observed weight increases result from initial oxidation of the BN framework.<sup>23</sup> These studies show that materials prepared at temperatures as low as 650 °C (12 h) are stable

(22) (a) *Gmelin Handbuch der Anorganischen Chemie, Boron Nitride. B-N-C Heterocycles. Polymeric B-N Compounds*; Springer-Verlag: New York, 1974; Vol 13, Part 1; pp 1–87. (b) Schwetz, K. A.; Lipp, A. In *Ullmann's Encyclopedia of Industrial Chemistry*; VCH: Deerfield Beach, 1985; Vol A4, pp 295–307.

(23) At higher temperatures (>1050 °C) a weight decrease is observed owing to vaporization of  $\text{B}_2\text{O}_3$ . See: Alekseev, A. F.; Lavenko, V. A.; Neshpor, V. S.; Frantsevich, I. N. *Dokl. Akad. Nauk. SSSR* 1978, 238, 370–373.



**Figure 5.** SEM (X2500) of PRD-166 ( $\text{Al}_2\text{O}_3/\text{ZrO}_2$ ) fibers: (a) uncoated fibers, (b) fiber dip-coated in 1 M (18% w/w) solution of  $(\text{CH}_3)_2\text{S-BHBr}_2$  and pyrolyzed under  $\text{NH}_3$  to 1000 °C.

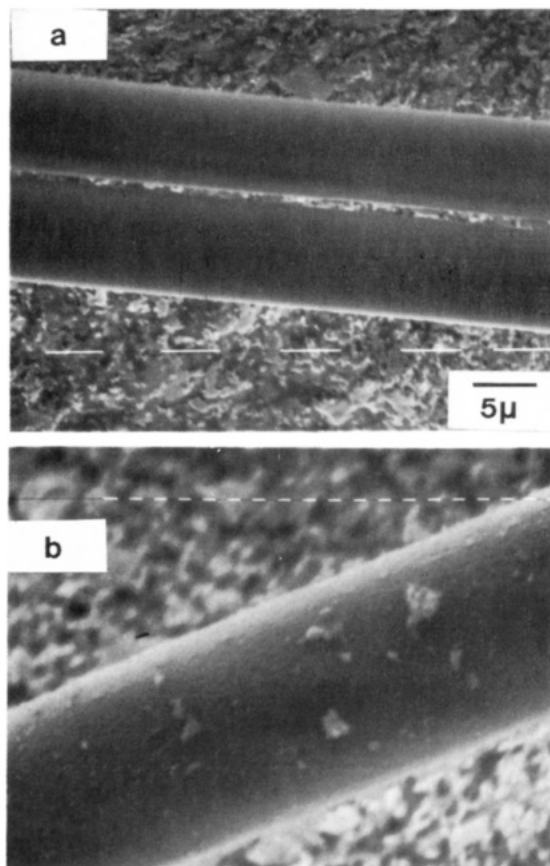


**Figure 6.** AES of BN coated PRD-166 fiber that had been dip-coated in 1 M (18% w/w) solution of  $(\text{CH}_3)_2\text{S-BHBr}_2$  and pyrolyzed under  $\text{NH}_3$  to 1000 °C.

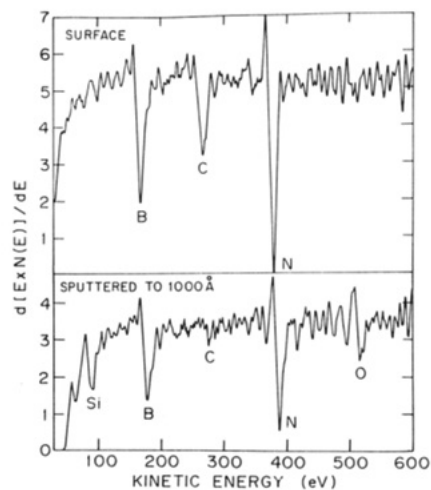
to air oxidation to at least 820 °C. Materials prepared at higher temperatures exhibit increased oxidative stability, with the 1500 °C (14 h) sample showing oxidation only above 940 °C. These results are consistent with both the increase in purity and the lattice organization indicated by the IR, XRD, and density measurements. Materials prepared from longer pyrolysis reactions (~60 h) do not exhibit a significant increase in oxidative stability. For example, the onset of air oxidation of the 60-h, 1500 °C sample was 960 °C.

**Fiber Coatings.** The conversion of  $(\text{CH}_3)_2\text{S-BHBr}_2$  to BN on the surfaces of two types of ceramic fibers was explored.

**$\text{Al}_2\text{O}_3/\text{ZrO}_2$  (Du Pont PRD-166).** As discussed in the Experimental Section, single fibers were dip-coated in a 1 M (18% w/w) solution of  $(\text{CH}_3)_2\text{S-BHBr}_2$  in  $\text{CH}_2\text{Cl}_2$  and pyrolyzed under  $\text{NH}_3$  to 1000 °C. SEMs of coated and uncoated single fibers are shown in Figure 5. A uniform



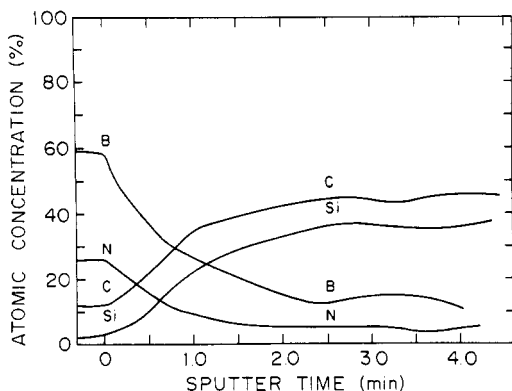
**Figure 7.** SEM of Nicalon SiC fibers: (a) uncoated fiber (X1250) (b) fiber (X2500) that has been dip-coated in 1 M (18% w/w) solution of  $(\text{CH}_3)_2\text{S-BHBr}_2$  and pyrolyzed under  $\text{NH}_3$  to 1000 °C.



**Figure 8.** AES of Nicalon SiC fibers dip-coated in 1 M (18% w/w) solution of  $(\text{CH}_3)_2\text{S-BHBr}_2$  and pyrolyzed under  $\text{NH}_3$  to 1000 °C: (a) surface; (b)  $\text{Ar}^+$  ion sputtered to 1000 Å.

BN coating of ~0.2–0.4 μm is clearly evident in Figure 5b. Confirmation of the nature of the coated material was obtained by AES as shown in Figure 6. The spectrum reveals major peaks at 179 (B) and 379 eV (N) with low levels of C (272 eV) and O (510 eV). Further study of the fiber showed the coating to be uniform over the entire fiber surface. A sputter depth profile of the coating indicated an approximate thickness of 2500 Å.

Coating of fiber bundles was accomplished by dipping fiber yarn in 7% w/w solutions of  $(\text{CH}_3)_2\text{S-BHBr}_2$  in  $\text{CH}_2\text{Cl}_2$ . The resulting fiber bundles displayed even coatings of BN on the individual fibers as determined by SEM. An AES depth profile indicated a thickness of



**Figure 9.** AES depth profile of Nicalon SiC fibers that have been dip-coated in  $\sim 0.1$  M (2% w/w) solution of  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2$  and pyrolyzed under  $\text{NH}_3$  to  $1000^\circ\text{C}$ .  $\text{Ar}^+$  sputtering rate =  $125 \text{ \AA}/\text{min}$ .

700–1000  $\text{\AA}$  for these coatings. BN coatings formed from higher concentrations of precursor usually resulted in the formation of BN aggregates interbridging between fibers.

**SiC (Nicalon).** Coated single fibers (18% w/w solution) were examined in a procedure similar to that described above. Again, evidence of a coating of BN is clearly visible in the SEM (Figure 7b). In addition, several areas containing BN aggregates are also apparent. The Auger spectrum of a BN coated SiC fiber is shown in Figure 8. Analysis of the surface showed the presence of B and N and an additional smaller peak for C.  $\text{Ar}^+$  ion sputtering to 1000  $\text{\AA}$  gave the expected B and N peaks and addi-

tionally Si (92 eV) and O (510 eV) peaks indicative of slight penetration into the fiber core. Coating of SiC fiber bundles was accomplished by dip-coating a fiber bundle in 2% w/w solutions of  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2$  in  $\text{CH}_2\text{Cl}_2$ . The resulting fibers were examined by SEM, which indicated a thin coating of BN at the surface. A depth profile study (Figure 9) indicated a coatings of approximately 250  $\text{\AA}$ .

In summary, the  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2/\text{NH}_3$  system offers a simple method for the preparation of boron nitride ceramics that has a number of unique advantages over either conventional CVD routes or known chemical precursors for the formation of boron nitride coatings. Thus, as demonstrated by the results discussed above, BN coatings of 125–2500  $\text{\AA}$  can be readily formed on either  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  or SiC fibers by varying the concentrations of the coating solutions. Preliminary work has demonstrated similar coating on smooth Sumitomo alumina fibers. Furthermore, with this method turbostratic boron nitride having oxidative stability to at least  $820^\circ\text{C}$  in air may be produced by precursor pyrolyses carried out as low as  $650^\circ\text{C}$ . We are currently exploring applications of this precursor and other III–V Lewis acid–base complexes for the formation of III–V ceramic coatings on a variety of substrates.

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**Registry No.**  $(\text{CH}_3)_2\text{S}\cdot\text{BHBr}_2$ , 55671-55-1;  $\text{NH}_3$ , 7664-41-7; BN, 10043-11-5.

## Defect Formation in Ag(I)–, Pb(II)–, Sn(II)–, and Bi(III)– $\beta''$ -Aluminas

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Ion exchange can be used to synthesize many mono-, di-, and trivalent isomorphs of the well-known fast ionic conductor Na(I)– $\beta''$ -alumina, among them the Ag(I)–, Sn(II)–, Pb(II)–, and Na(I)–Bi(III) forms. These four compositions normally are colorless and electronically insulating, but they become purple semiconductors when heated to approximately  $650^\circ\text{C}$  in a low partial pressure of oxygen. They are very hygroscopic, and coloration occurs only if samples have been partially hydrated prior to the high-temperature treatment but not if they are first dried carefully at elevated temperature in a dry oxygen atmosphere. The optical absorption arises from metal clusters formed during the dehydration process in the conduction layers. In single crystals, the coloration reaction is reversible and no bulk decomposition can be detected. However, powdered samples of Pb(II)– $\beta''$ -alumina treated at  $650^\circ\text{C}$  in 15%  $\text{H}_2/85\%$   $\text{N}_2$  have been shown to decompose into a mixture of lead metal and other products of the partial decomposition of  $\beta''$ -alumina. The results underscore the great sensitivity of the various  $\beta''$ -aluminas to hydration, a phenomenon that must be considered in any careful study of the structures and properties of these materials.

### Introduction

Na(I)– $\beta''$ -alumina, a well-known fast ionic conductor of Na(I) ions, has the general formula,  $\text{Na}_{1+x}\text{Mg}_x\text{Al}_{11-x}\text{O}_{17}$ , where  $x$  is about 0.67. The rapid cation diffusivity in this compound makes it possible to replace its entire Na(I) content with a wide variety of mono-, di-, and trivalent cations by relatively simple ion-exchange reaction.<sup>1,2</sup> This

remarkable ion-exchange chemistry provides a route to the synthesis of many unusual materials, some of which have been shown to have potential applications as solid electrolytes<sup>3</sup> and solid-state lasers.<sup>4</sup>

The optical and electrical properties of several  $\beta''$ -alumina isomorphs have been found to change during heating

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