

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

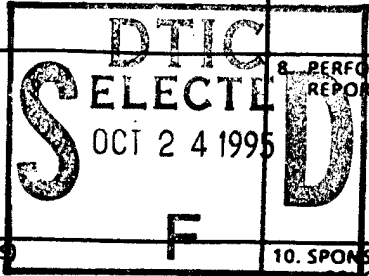
Please reduce the burden for this collection of information by estimating to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (10704-0188) Washington, DC 20503

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE June 26, 1995	3. REPORT TYPE AND DATES COVERED Final 5-1-92-4-30-95
----------------------------------	---------------------------------	--

4. TITLE AND SUBTITLE Chemistry of Borane Anions: Formation Of Precursors And Their Conversion To Boron Aluminum Nitrides And Metal Borides	5. FUNDING NUMBERS DAAL03-92-G-0199
--	--

6. AUTHOR(S) Sheldon G. Shore

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Ohio State University Research Foundation 1960 Kenny Rd. Columbus, Ohio 43201	8. PERFORMING ORGANIZATION REPORT NUMBER
--	--



9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARO 29560.10-CH
--	---

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.	12b. DISTRIBUTION CODE
--	------------------------

ABSTRACT (Maximum 200 words)

Additional evidence was obtained for the formation $[BH_3]^{2-}$ and $[B_2H_6]^{2-}$ and the sequence in which they are formed. The fluxional nature of the anion $[B_{10}H_{11}]^-$ was examined by NMR spectroscopy and a single crystal X-ray analysis of data obtained at $-150\text{ }^\circ\text{C}$ revealed the presence of two fluxional isomers. An X-ray analysis proved the structure of $[2-CH_3CNB_{10}H_9]^-$. An X-ray structure of $[Al(BH_4)_4]_3^-$ showed the presence of eight Al-H-B bonds, a rare example of eight-coordinate aluminum. A unique example of a stable charge transfer complex $[B_{10}H_{14}]^-$ was characterized in the solid state and in solution. Improved syntheses of lanthanide boranes were developed. A new morphology of BN nitride, a tubular form was prepared. Evidence was obtained for a possible mechanism by which this material is formed from amorphous BN is produced from the reaction of Cs with $B_3H_3N_3Cl_3$. AlN-BN composites were produced by a new method, and studies were initiated on the preparation of AlN powders and films.

14. SUBJECT TERMS borane anions, aluminum borohydride anions, decaborane, lanthanide borides, BN, AlN, AlN-BN composites	15. NUMBER OF PAGES 20
---	---------------------------

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL
---	--	---	----------------------------------

NSN 7540-01-280-5500

DTIC QUALITY INSPECTED 1

19951023 034

**CHEMISTRY OF BORANE ANIONS: FORMATION OF PRECURSORS
AND THEIR CONVERSION TO BORON ALUMINUM NITRIDES AND
METAL BORIDES**

**Sheldon G. Shore
Final Report**

**For the Period
May 1, 1992 - April 30, 1995**

June 26, 1995

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

**U. S. ARMY RESEARCH OFFICE
Research Triangle Park, North Carolina 27709**

**ARO Proposal No. 29560-CH
GRANT No. DAAL03-92-G-0199**

The Ohio State University Research Foundation

**APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.**

THE VIEWS OPINIONS, AND/OR FINDINGS CONTAINED IN THIS REPORT
ARE THOSE OF THE AUTHOR AND SHOULD NOT BE CONSTRUED AS AN
OFFICIAL DEPARTMENT OF THE ARMY POSITION, POLICY, OR DECISION,
UNLESS SO DESIGNATED BY OTHER DOCUMENTATION

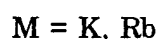
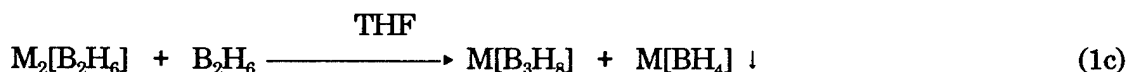
FORWARD

This program has been concerned with several aspects of synthetic inorganic chemistry. We continued to develop the fundamental chemistry of borane anions and we expanded our efforts in aluminum hydride-boron hydride chemistry. Furthermore, we made appreciable progress in potentially practical aspects of materials chemistry. These include new and improved syntheses of precursors to the formation of lanthanide borides; the discovery of a previously unrecognized morphology of boron nitride, a tubular form; a new method for the formation of AlN-BN composites; and the preparation of aluminum nitride films and powders. While our program has been diverse, it should be recognized that there is a common thread of techniques and chemistry which enabled us to successfully direct our attention in several directions.

CONTENTS

Forward	i
Contents	ii
I. Reduction of BH_3 to $[\text{BH}_3]^{2-}$ and the Formation of $[\text{B}_2\text{H}_6]^{2-}$	1
II. Protonation of <i>closo</i> - $[\text{B}_{10}\text{H}_{10}]^{2-}$	2
III. Synthesis and Structure of Triethylammonium Acetonitrilenonahydro <i>closo</i> -decaborate(-1)	3
IV. Iodide Charge Transfer Complexes of Decaborane(14) and 2,4-Diiododecaborane(14)	5
V. Synthesis and Structure of $[\text{Ph}_3\text{MeP}][\text{Al}(\text{BH}_4)_4]$, and an Eight-Coordinate Aluminum(III)	6
VI. Syntheses of New Yb(II) and Eu(II) Boranes	7
VII. A New Morphology of Boron Nitride a Tubular Form	8
VIII. Possible Mechanism for the Formation of Tubular Form of BN	11
IX. A New Method for the Formation of AlN-BN Composites	13
X. Aluminum Nitride Films and Powders	14
XI. Publications, Patent, Dissertations	17
XII. Participating Scientific Personnel	18
XIII. Report of Inventions	18
XIV. Bibliography	18

I. Reduction of BH_3 to $[\text{BH}_3]^{2-}$ and the Formation of $[\text{B}_2\text{H}_6]^{2-}$. During the grant period we improved¹ upon our earlier evidence for the existence of $[\text{BH}_3]^{2-}$ and $[\text{B}_2\text{H}_6]^{2-}$, the isoelectronic analogues of $[\text{CH}_3]^-$ and C_2H_6 , respectively. Such species, as possibly generated in the reduction of diborane,^{2,3} have been the subjects of discussion and speculation since the work of Stock² in 1935. Boron-11 NMR spectra reveal the sequential formation of $[\text{BH}_3]^{2-}$ and $[\text{B}_2\text{H}_6]^{2-}$ as stable intermediates in the reaction of B_2H_6 with alkali metal (K or Rb) naphthalides to form $[\text{B}_3\text{H}_8]^-$ and $[\text{BH}_4]^-$ as the final products. These species were observed upon addition of increments of B_2H_6 to alkali metal naphthalide in THF solutions (Equations (1a)-(1c)). Boron-11 NMR spectra are given in Figure 1.



When B_2H_6 is added in a 1:4 ratio to a potassium or rubidium naphthalide solution (Equation (1a)) a quartet (1:3:3:1) is observed in the ^{11}B NMR spectrum (Figure 1a) that is assigned to $[\text{BH}_3]^{2-}$. Addition of B_2H_6 to this solution (Equation (1b)) results in the appearance of a second quartet (1:3:3:1) at higher field (Figure 1b) that is assigned to $[\text{B}_2\text{H}_6]^{2-}$. Complete consumption of $[\text{BH}_3]^{2-}$ to form $[\text{B}_2\text{H}_6]^{2-}$ is best achieved by titration of the solution containing $[\text{BH}_3]^{2-}$ with B_2H_6 . Figures 1b and 1c illustrate this conversion. Addition of B_2H_6 to a solution of $[\text{B}_2\text{H}_6]^{2-}$ (Equation (1c)), results in the formation of $\text{M}[\text{B}_3\text{H}_8]$, identified by its characteristic ^{11}B NMR signal at -30.1 ppm, (Figure (1)) and $\text{M}[\text{BH}_4]$ that forms as a precipitate. There is no evidence in the NMR spectra for intermediate species during the conversion of $[\text{B}_2\text{H}_6]^{2-}$ to $[\text{B}_3\text{H}_8]^-$ and $[\text{BH}_4]^-$. Addition of excess B_2H_6 at any point during the reaction series shown in Equations (1a)-(1c) results in consumption of the intermediate species and the formation of $\text{M}[\text{B}_3\text{H}_8]$ and $\text{M}[\text{BH}_4]$, as a precipitate, and borane as BH_3THF (Figure (1e)). Soluble side products are naphthyl borohydrides.⁴

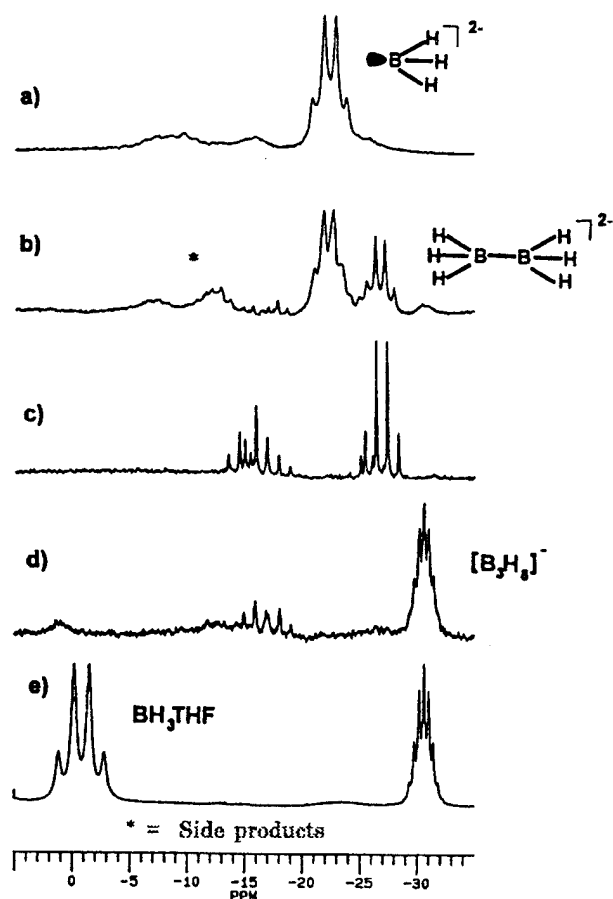


Figure 1. Boron-11 NMR spectra in THF at 303 K.

II. Protonation of *closo*- $[\text{B}_{10}\text{H}_{10}]^{2-}$. It has been shown that protonation of $[\text{B}_{10}\text{H}_{10}]^{2-}$ results⁵ in the formation of $[\text{B}_{10}\text{H}_{11}]^-$. While published NMR studies are limited,^{5,6} they reveal that the hydrogen atoms of $[\text{B}_{10}\text{H}_{11}]^-$ are highly fluxional. Published⁷ X-ray studies of salts of this anion have been frustrated by problems of disorder.

Relatively recently an *ab initio*/IGLO study of the structure and nonrigidity of $[\text{B}_{10}\text{H}_{11}]^-$ were reported.⁸ In view of the more modern instrumentation available to us than to the earlier investigators, it was of interest to test the conclusions drawn from this theoretical study. We examined in detail variable temperature ^{11}B and ^1H NMR spectra, 2D COSY ^{11}B - ^{11}B , and NOESY ^{11}B - ^{11}B $[(\text{Ph}_3\text{P})_2\text{N}][\text{B}_{10}\text{H}_{11}]$. We were also able to determine the structure of $[(\text{Ph}_3\text{P})_2\text{N}][\text{B}_{10}\text{H}_{11}]$ from single crystal X-ray data obtained at

-150 °C.

The X-ray structure determination of $[(\text{Ph}_3\text{P})_2\text{N}][\text{B}_{10}\text{H}_{11}]$ revealed that it crystallizes with two independent molecules in the unit cell. The structures of the two independent $[\text{B}_{10}\text{H}_{11}]^-$ ions are shown in Figure 2. The eleventh hydrogen atom in structure (a) bridges three boron atoms in the polar cap, an apical boron atom and two equatorial boron atoms. On the other hand the eleventh hydrogen atom in structure (b) bridges the equatorial belt between the two polar regions. These isomeric structures of $[\text{B}_{10}\text{H}_{11}]^-$ are supportive of the fluxional isomers that have been proposed on the basis of the *ab initio*

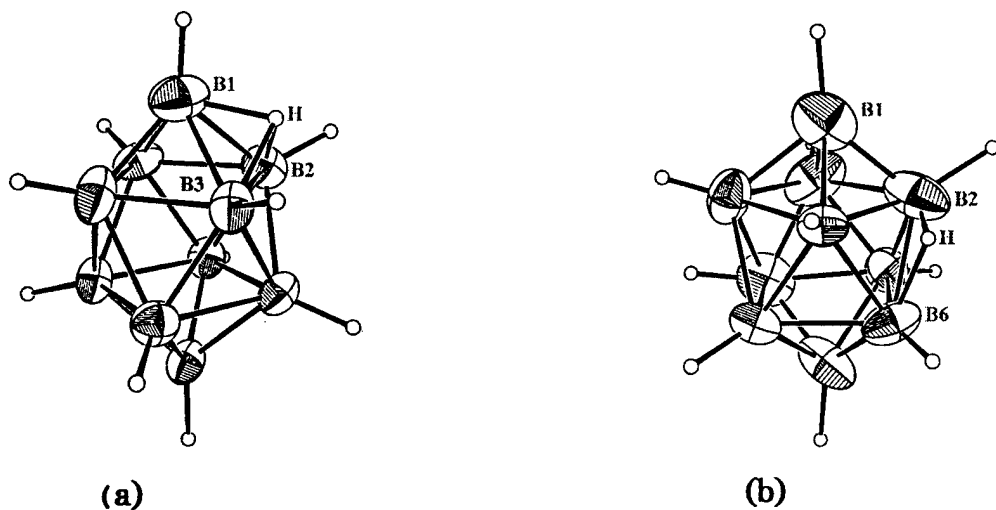
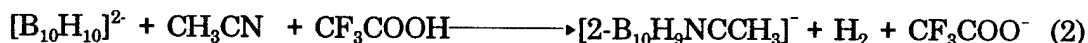


Figure 2. Structures of $[\text{B}_{10}\text{H}_{11}]^-$ isomers.

calculations. They support interpretations of NMR spectra that propose rapid migration of the unique hydrogen around the polar cap and also a migration between the polar caps via a μ_2 bridge across the equatorial belt regions. Our NMR studies indicate that the barrier for rapid migration of the eleventh proton between the two polar regions is 17 Kcal/mol. The calculated barrier is 19 Kcal/mol.⁸

III. Synthesis and Structure of Triethylammonium 2-Acetonitrile-nonahydro-closo-decaborate(-1). Acid-mediated hydride displacement on $[\text{B}_{10}\text{H}_{10}]^{2-}$ by substituents containing O, S, and N as donating elements has been described.⁹ We found¹⁰ that $[\text{Et}_3\text{NH}][2\text{-B}_{10}\text{H}_9\text{NCCH}_3]$ is formed from the reaction of $[\text{Et}_3\text{NH}]_2[\text{B}_{10}\text{H}_{10}]$ with CH_3CN solution at 60 °C. in the presence of CF_3COOH . Subsequent recrystallization from CH_3CN yielded $[\text{Et}_3\text{NH}][2\text{-B}_{10}\text{H}_9\text{NCCH}_3]$ in better than 90% yield. Isomeric species were not

detected by NMR spectroscopy. Similar reaction of $K_2[B_{10}H_{10}]$ with CF_3COOH in CH_3CN solution resulted in the formation of $K[2-B_{10}H_9NCH_3]$ (Equation (2)).



The structure of $[Et_3NH][2-B_{10}H_9NCCH_3]$ was determined. The anion (Figure 3) is a bicapped square-antiprism with CH_3CN coordinated through the N atom to one equatorial boron atom. The ^{11}B NMR spectrum is fully consistent with the X-ray structure of the anion.

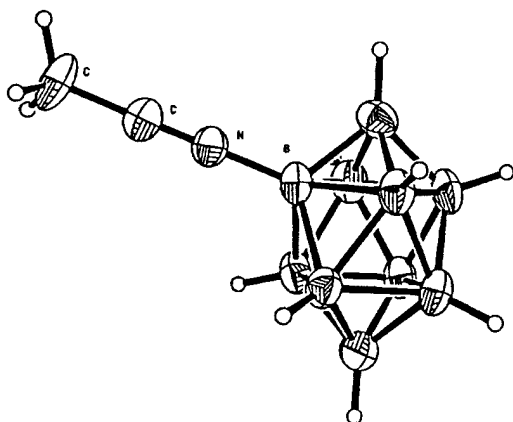
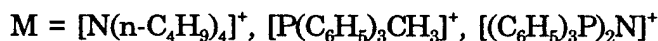


Figure 3. Structure of $[2-B_{10}H_9NCCH_3]^-$.

Earlier, a similar hydride displacement reaction as Equation (2) was proposed as a possible secondary reaction in a kinetic study of the reaction of $[B_{10}H_{10}]^{2-}$ with benzoylating agents in the presence of CF_3COOH .¹¹ However, the product was not characterized and no structure was proposed. Based upon the ^{11}B NMR spectrum at 19.25 MHz another earlier study reported that $[B_{10}H_{10}]^{2-}$ in the presence of *p*-toluenesulfonic acid forms $[1-B_{10}H_9NCCH_3]^-$ in refluxing CH_3CN solution^{9c}. We repeated the synthesis and ^{11}B NMR spectra at 80.25 MHz revealed that the $[2-B_{10}H_9NCCH_3]^-$ isomer is the only isomer detected. A number of apically and equatorially substituted isomers of $[B_{10}H_{10}]^{2-}$ have been reported with the site of substitution being dependent upon the reaction conditions employed. Possibly other misassignments also occurred in earlier work in which structural characterization was based primarily upon NMR studies at relatively low field strengths.

IV. Iodide Charge Transfer Complexes of Decaborane(14) and 2,4-Diiodo-decaborane(14). Work on iodide charge transfer complexes of $B_{10}H_{14}$ and 2,4- $I_2B_{10}H_{12}$ initiated during an earlier grant period was completed during the present grant period.¹²

We formed complexes of the general molecular formula $[M][B_{10}H_{14}I]$ (Equation (3)). The stabilities of these complexes are highly dependent upon the choice of cation. With

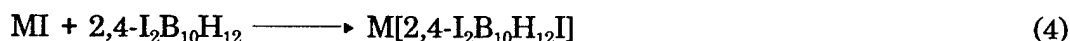


large cation iodides, products form upon mixing of the solid reactants. Addition of THF or CH_2Cl_2 produces deep yellow solutions. These complexes are isolated as solid, air stable materials. The decaborane(14) molecule is tightly bound in the solids. Once the complex is formed and the solvent is removed, decaborane(14), which is normally volatile at room temperature cannot be sublimed from the complex even at 95 °C under vacuum (10^{-3} Torr).

The $[B_{10}H_{14}I]^-$ ion absorbs in the visible region at 355 nm in CH_2Cl_2 . The position of the maximum is independent of the cation and the sample concentration. Formation of $[(n-C_4H_9)_4N][B_{10}H_{14}I]$ in CH_2Cl_2 was followed by a continuous variations titration experiment in which the absorbance maximum of the complex was monitored. A plot of absorbance vs. mole fraction of $[(n-C_4H_9)_4N]I$ gave a well defined maximum at a mole fraction of 0.5. This is consistent with a combining ratio of 1:1, in accord with Equation (3).

The general appearance of the ^{11}B spectrum of $[(C_6H_5)_3P)_2N][B_{10}H_{14}I]$ resembles that of $B_{10}H_{14}$ and is consistent with apparent C_{2v} point symmetry of the B_{10} cage. However, the resonances are shifted from those of $B_{10}H_{14}$.

The $[B_{10}H_{10}I]^-$ is disordered in its crystalline salts. However, the substituted decaborane 2,4- $I_2B_{10}H_{12}$ readily forms crystalline $M[2,4-I_2B_{10}H_{12}I]^-$ Equation (4) .



The molecular structure of $[2,4-I_2B_{10}H_{12}I]^-$ was determined as the $[P(C_6H_5)_3CH_3]^+$ salt (Figure 4). The iodide ion rests on the open face of the B_{10} basket. A space filling representation of complex is given in Figure 5. The iodide ion-bridging hydrogen distances, 2.99(7)-3.11(7) Å is less than or equal to the sum of the van der Waals radii (3.2- 3.6 Å).

Decaborane(14) is a polar (*ca.* 3 Debye), electron deficient molecule that readily accepts one and two electrons. The reaction of this molecule and the related molecule 2,4- $I_2B_{10}H_{12}$ with I^- presumably occurs through transfer of electron density from the I^- to the LUMO of the decaborane. While alkali metal iodides, NaI and KI, react with $B_{10}H_{14}$ in solution, removal of solvent results in dissociation into the alkali metal iodide and decaborane components. This dissociation is believed to reflect the relatively large lattice energies of the alkali metal iodides compared to those of the iodide salts of the complex cations ($[N(n-C_4H_9)_4]^+$, $[P(C_6H_5)_3CH_3]^+$, $[(C_6H_5)_3P)_2N]^+$).

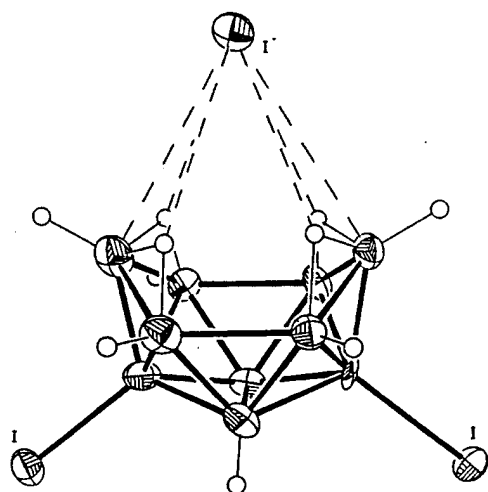


Figure 4. Structure of $[2,4-I_2B_{10}H_{12}]^-$.

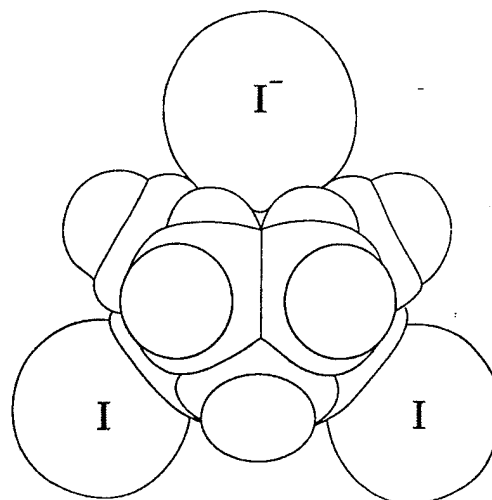
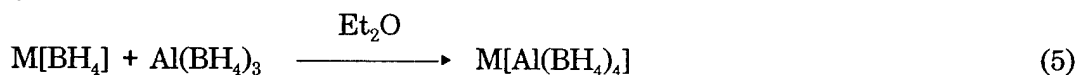


Figure 5. Space filling representation of $[2,4-I_2B_{10}H_{12}]^-$.

V. Synthesis and Structure of $[Ph_3MeP][Al(BH_4)_4]$, an Eight-Coordinate Aluminum(III). The aluminum borohydride anion $[Al(BH_4)_4]^-$ is of interest because it is a very strong reducing agent and the coordination geometry around the central aluminum atom with respect to the number 3 center 2 electron Al-H-B bridge bonds present was unknown prior to our work. Although this anion was studied earlier,¹³ characterizations of its salts stabilized by large complex cations was incomplete. We prepared salts of $[Al(BH_4)_4]^-$ through Equation (5)¹⁴ in a procedure more effective than an earlier reported method.¹³





Extensive NMR studies ^1H , ^{11}B , and ^{27}Al were carried out on these salts in CD_2Cl_2 solution. They are thermally stable above 100°C . The structure of $[\text{Ph}_3\text{MeP}][\text{Al}(\text{BH}_4)_4]$ was determined. The structure of $[\text{Al}(\text{BH}_4)_4]^-$ (Figure 6) consists of a central aluminum atom surrounded by four BH_4 groups arranged as a distorted tetrahedron. Two of the four hydrogen atoms around each boron form hydrogen bridges with the aluminum atom. These eight bridging hydrogens that surround the aluminum center establish a slightly distorted dodecahedral coordination geometry (Figure 7). This is believed to be the first reported¹⁴ structure of a molecular entity with eight coordinate aluminum(III). Although $[\text{Al}(\text{BH}_4)_4]^-$ possesses apparent 2-electron, 3-center hydrogen bridges, there is probably significant ionic interaction between the aluminum center and borohydride groups.

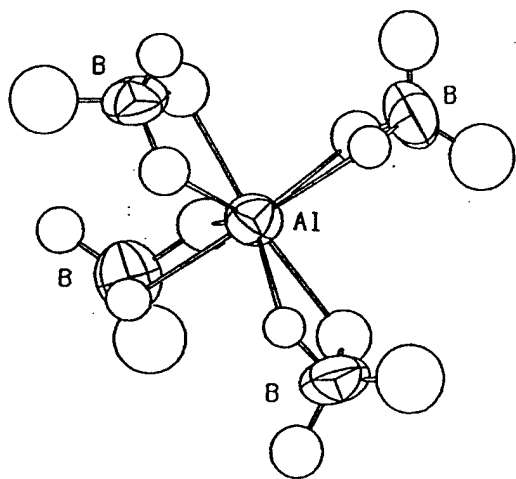


Figure 6. Structure of $[\text{Al}(\text{BH}_4)_4]^-$.

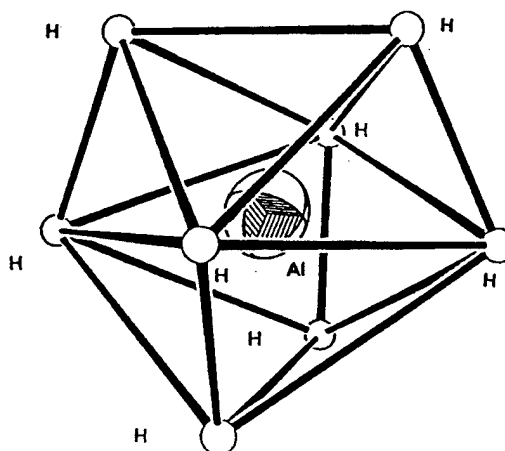
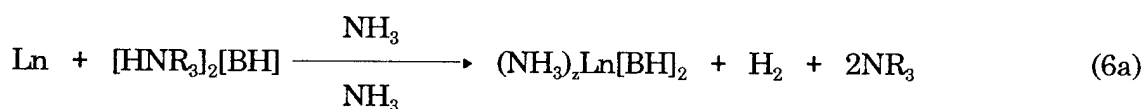
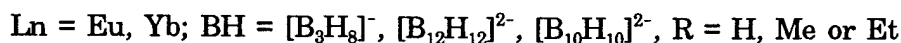


Figure 7. Dodecahedral arrangement of H atoms in $[\text{Al}(\text{BH}_4)_4]^-$.

VI. Syntheses of Yb(II) and Eu(II) Boranes. During the present grant period new Yb(II) and Eu(II) complexes of $[\text{B}_3\text{H}_8]^-$ and $[\text{B}_{12}\text{H}_{12}]^{2-}$ were prepared by reduction of ammonium salts of boron hydride anions with elemental Yb and Eu in liquid ammonia in (Equation (6)). This type of reaction was also employed for the preparation of our previously





reported^{17,18} lanthanide complexes of $[\text{B}_{10}\text{H}_{10}]^{2-}$ and $[\text{BH}_4]^{-}$ and supersedes earlier syntheses.

The new complexes have not yet been characterized structurally, but when the products of these reactions are desolvated, IR spectra indicate the presence of Ln-H-B bridges.

VII. A New Morphology of Boron Nitride a Tubular Form. Boron nitride possesses a number of useful properties and articles composed (wholly or in part) of BN are finding an increasing number of applications. There is consequently great interest in finding new and improved methods for its production.¹⁵

Under earlier ARO support we developed a relatively low-temperature procedure for the formation of an amorphous preceramic form of boron nitride through the reaction of B-trichloroborazine, $\text{B}_3\text{Cl}_3\text{N}_3\text{H}_3$, with an alkali metal in the absence of a solvent.¹⁶ The reaction is an explosive one that is initiated at temperatures as low as 125 °C when Cs is the alkali metal. The reaction is easily contained in a thick-walled glass pressure vessel. The resulting preceramic BN is a finely divided powder which is readily separated from by-products of this reaction; XRD indicates that it is amorphous.

Upon pyrolysis at 1100 °C the preceramic BN is converted to turbostratic BN (a partially ordered pseudographitic form). SEM reveals that it exists in two distinct morphologies. In addition to the commonly observed distorted lamellar morphology, hollow tubular structures are also formed.

The distorted lamellar crystallites (Figure 8) are consistent with the partially ordered turbostratic form of BN. The second type of BN (Figure 9) consists of hollow tubular structures, the largest of which are 5 μm in diameter, with a length of 150 μm . In general diameters are 3-4 μm with lengths of 50-100 μm . The walls of the larger tubes have a thickness of up to 1000 Å. It is of interest that the tubes appear to be aligned in a parallel orientation (Figure 9), and most have a closed rounded end.

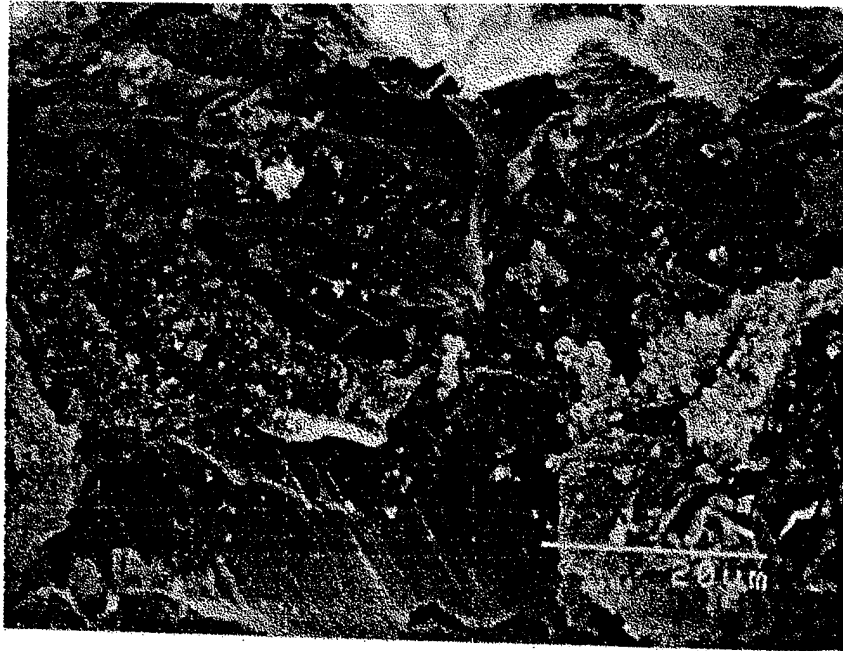


Figure 8. SEM of lamellar BN morphology.

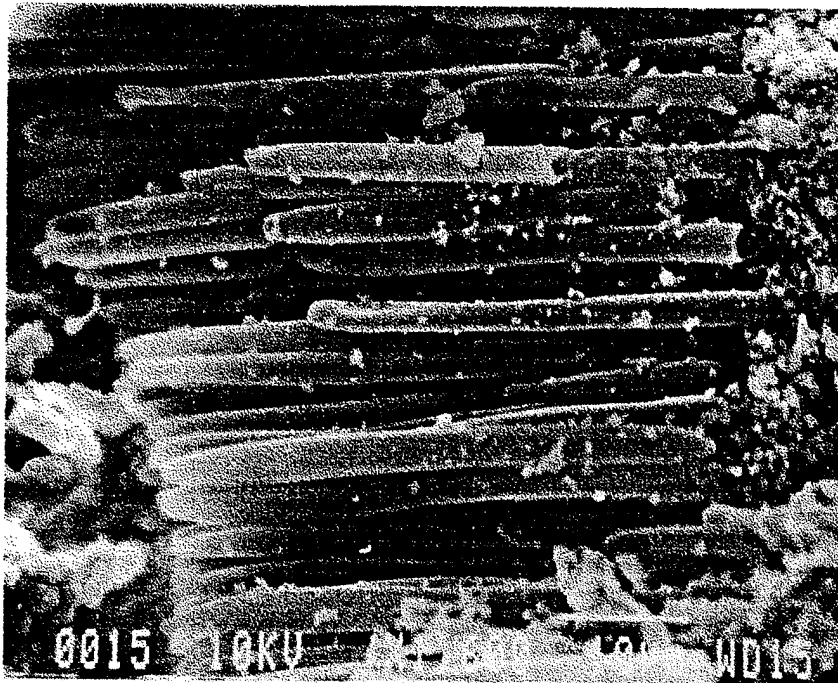


Figure 9. SEM of a group of BN tubules.

Reports from "Fullerene", C_{60} syntheses also describe needle like graphitic carbon structures¹⁹ and concentric "onion like" carbon tubes in which layered sheets of graphite hexagons are rolled into tubes.²⁰ These graphitic structures are two orders of magnitude smaller than the structures described here. Filaments, tubes, and shells of carbon have also been formed as a result of decomposition of organic gases on supported metal (predominantly Ni) catalyst particles.²¹ Electron microscopy reveals the presence of metal or metal oxide particles at the ends of or filling the carbon structures. In the case of BN presented here, however, no such catalysts were used or detected.

TEM (Figures 10 and 11) of the turbostratic material (tubular and lamellar) reveals several features. Selected-area diffraction from a single tube wall of ca. 300 Å thickness further indicates that the tubular BN is also turbostratic. The electron diffraction patterns for all morphologies correspond closely to the X-ray diffraction pattern of turbostratic BN and can be indexed by reference to the XRD pattern of hexagonal BN. The highlighted circle in Figure 11a shows the region from which the diffraction pattern. Figure 11b was obtained from the wall of a tube.

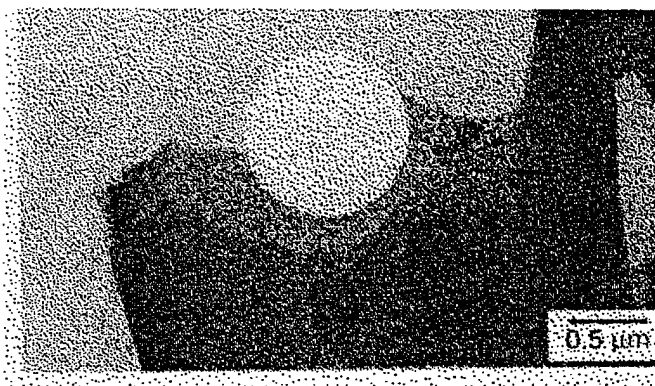


Figure 11a. TEM of BN tube fragment. Highlighted area shows the region from which the electron diffraction pattern was obtained.

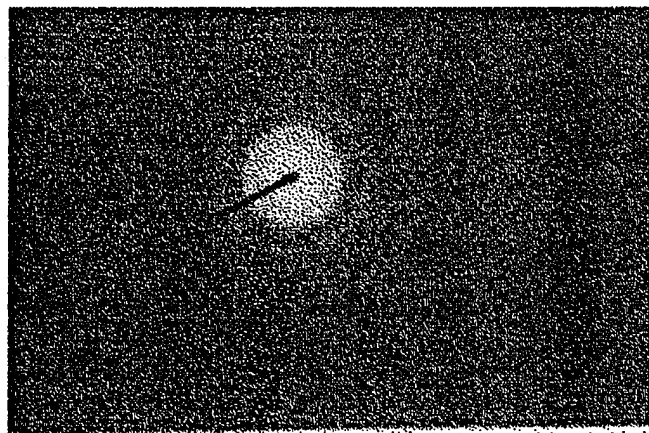


Figure 11b. Electron diffraction pattern. Rings correspond to diffraction of [002], [10], and [110] planes of hexagonal BN.

A high-resolution TEM micrograph from a single tube wall (Figure 12) shows the pseudographitic stacking. The observed interlayer spacing is ca. 3.5 Å. However, only local order exists within the wall. Boundaries are readily observable between grains of ca. 20 Å on edge, and the grains adopt an apparently random orientation with respect to one another. This is entirely consistent with the ED pattern obtained.

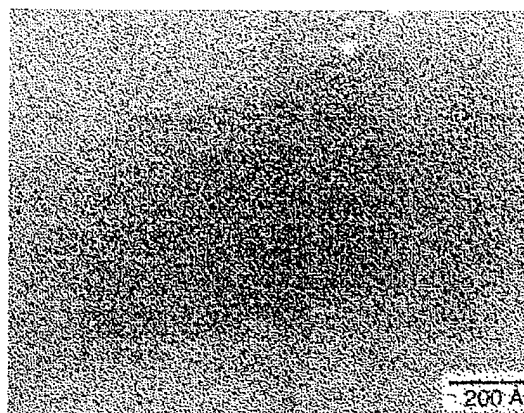


Figure 12. High-resolution TEM from a region of a single tube wall.

VIII. Possible Mechanism for the Formation of the Tubular Form of BN.

High-resolution TEM images reveal the presence of tubular structures smaller than those shown in Figure 9. They have a typical diameter of $0.15 \mu\text{m}$. In close proximity to these are also observed flatter, "corpuscular" structures of similar diameter. It is possible that these corpuscles (Figure 13) are the sites of incipient growth of the tubes. The preferred parallel orientations of groups of fibers observed by SEM may be the result of their growth from a "field" of these "corpuscular structures" attached to a relatively flat surface. These "corpuscular seeds" may themselves be formed from small shell-like structures observed by TEM in the amorphous BN obtained. These shell like structures are discussed below.



Figure 13. TEM of BN corpuscles.

SEM images of the amorphous BN product after the removal of by-products, but prior to heat treatment at 1100 °C indicate the product to be largely unstructured (Figure 14a). However, TEM on this material at higher powers of resolution reveals the presence of shell-like pseudospherical structures that appear to be hollow in nature (Figure 14b). These hollow

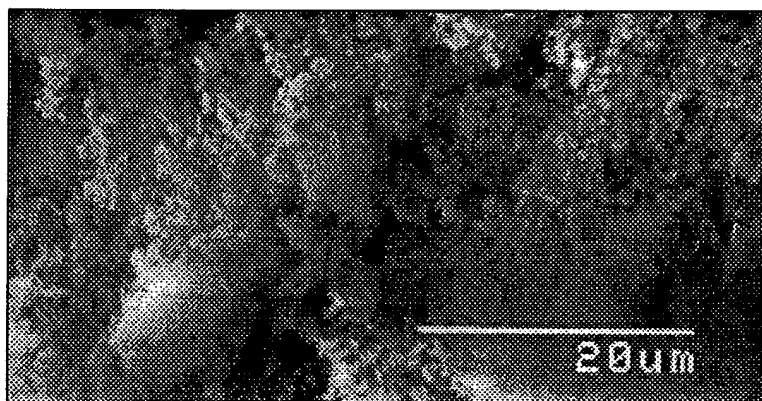


Figure 14a. SEM of amorphous BN.

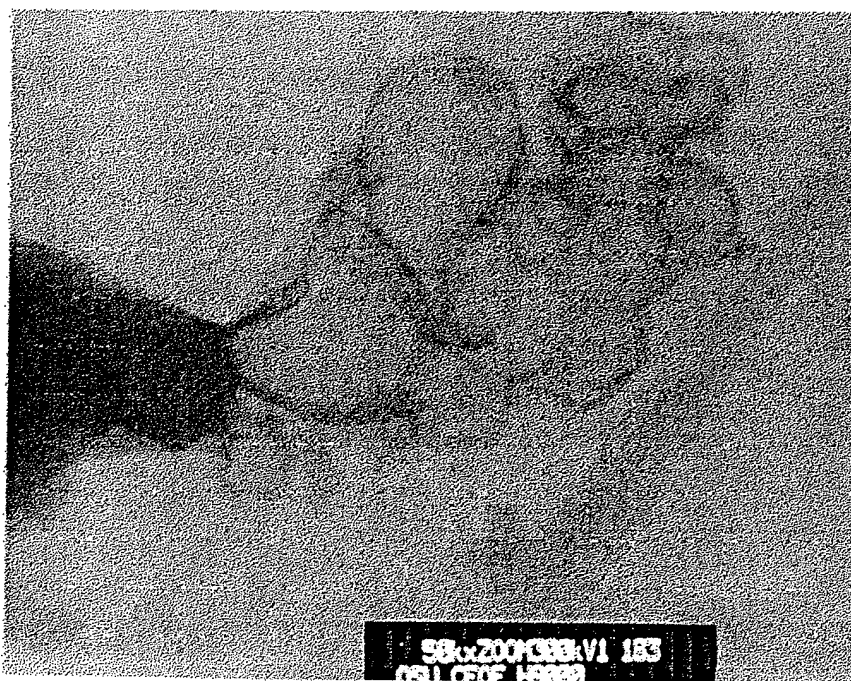


Figure 14b. High-resolution TEM of amorphous BN showing hollow shell-like structures. Note the partial collapse of the shell at the left of the image.

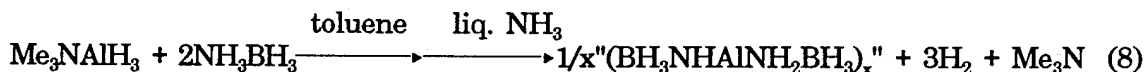
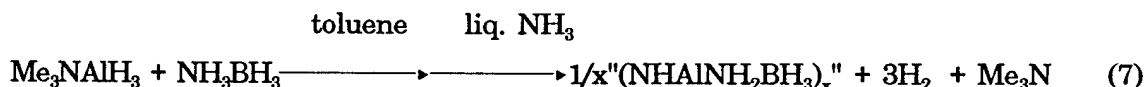
shells are typically a fraction of a μm in diameter, and are very thin walled, with a typical wall thickness of around 100 \AA . While the explosive reaction to prepare the preceramic amorphous BN is initiated at relatively low temperature, much higher temperatures are undoubtedly generated in the reaction. Given that the reaction results in a poorly ordered solid from molten precursors, it is possible that these shells result from bubbles caused by rapid expulsion of gaseous side products (HCl , H_2). Note, in Figure 14b that the structure at the left of the image appears to be undergoing collapse. It is possible that the "corpuscular" structures shown in Figure 13 are themselves a result of collapse at elevated temperatures of the shells observed in the amorphous material. Thus the corpuscles could be sites of tube growth. Formation of the hollow shells in the initial reaction is believed to be central to the ultimate formation of the novel tubular morphology, in that upon collapse, they provide nucleation centers for aggregation or sintering of small particles, thus facilitating an effective reduction of surface energy.

The formation of tubular structures from the preceramic amorphous material by a type of sintering mechanism would necessarily require some mobility of the amorphous precursor at the requisite temperature, in this case ca. $1100 \text{ }^\circ\text{C}$. This suggests that tube formation requires a relatively "local" supply of preceramic amorphous BN in the vicinity of the nucleation centers (or corpuscles). Growth orthogonal to the corpuscle surface would lead to a tube of diameter comparable to that of the corpuscle. Alternatively, initial growth outward from the corpuscle edge, thereby increasing its diameter, followed by onset of orthogonal growth at some favorable point would lead to a tubular structure with larger diameter than that of the initially-formed shell and corpuscle. In this regard, it is particularly interesting that a typical wall thickness of around 300 \AA is common to both the larger and smaller tubes. It may be that this wall thickness is optimal for both surface energy reduction and heat transfer phenomena.

IX. A New Method for the Formation of AlN-BN Composites. Dispersed-phase composite materials containing AlN and BN offer the promise of improved fracture toughness and resistance to wear and erosion by incorporation of a soft lubricating BN phase with hard and wear resistant AlN phase.²² In recent years, high thermal and shock resistant windows made from AlN-BN composite materials have been used for the protection of communication and detection equipment on aircraft.²³ Performance of these materials is highly dependant on their uniformly dispersed microstructures. However, such microstructures are difficult to

obtain through classical powder processing techniques. Recently, several precursors were developed to prepare these materials. In one procedure,²⁴ intimate mixtures of AlN and BN powders were prepared from the reactions of alkyl aluminum and borazine followed by pyrolysis. In another report, a homogeneous composite of turbostratic BN and crystalline AlN was obtained by pyrolysis of a precursor from the reaction of B(NEt₂)₃ with diethyl aluminum amide.²⁵ Mixtures of aluminum nitride and boron nitride were also prepared by decomposition of aluminum ammoniate borohydrides.

During the present grant period we developed a new method²⁶ for the preparation of AlN-BN ceramic mixtures which employs reactions of Me₃AlH₃ with NH₃BH₃. The reactions of Me₃AlH₃ with ammonia-borane, NH₃BH₃, in 1:1 and 1:2 ratios in toluene solutions followed by treatment with liquid ammonia produce polymeric preceramic precursors "(NHAlNH₂BH₃)_x" and "(BH₃NHAlNH₂BH₃)_x" (Equations (7) and (8)). These



preceramic precursors were characterized by IR, TGA, and solid state MAS ²⁷Al NMR spectroscopy. They were then converted into intimate ceramic AlN-BN mixtures in 45-60% yields via pyrolysis at 1000 °C (Equations (9) and (10)). The powder XRD patterns of the



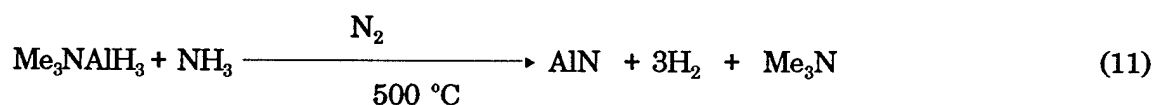
ceramic mixtures reveal the presence of the AlN wurzite phase and the BN hexagonal phase. The IR spectra of these mixtures show bands at 1400 and 810 cm⁻¹, characteristic of BN and a band at 703 cm⁻¹, characteristic of AlN. MAS ²⁷Al NMR spectra for AlN-BN mixtures show expected resonances for AlN phases and no oxide phases were detected.

Morphology of the ceramic powders of AlN/BN and AlN/2BN mixtures was examined by SEM and *in situ* EDS. Particles ranging in size from 5-50 μm are observed with smaller fragments of random sizes. The EDS study indicates that in both the 1:1 and 1:2 AlN-BN mixtures that the particles examined contain both AlN and BN.

X. Aluminum Nitride Films and Powders. Aluminum nitride, possesses a properties that make it "an increasingly important material in microelectronics, optoelectronics, and materials science".²⁷ It has high thermal conductivity, high electrical resistivity, high decomposition temperature with high resistance to oxidation, low thermal expansion coefficient which is a close match to that of Si and GeAs, and it is transparent in the visible and near infrared regions²⁸. Some applications for which it is suitable are as dielectric and passivation layers in microelectronic devices and coating material in optoelectronic devices.²⁹ Due to their high surface acoustic wave velocity and piezoelectric character³⁰ AlN films also have applications in surface acoustic wave devices and as high temperature, oxidation resistant, structural ceramic materials.

During the present grant period we initiated an effort to prepare AlN films and powders in a relatively simple way which would improve upon the existing chemical processes employed for CVD. We believe that the procedure we initiated will meet the requirements for electronic applications in that the AlN should have low oxygen, metallic, and carbon impurity contents. Our procedure for preparing powders is expected to provide a narrow and uniform particle size distribution.

Results we have obtained are preliminary at the present time, but they are extremely promising. AlN films were deposited on quartz plates at 500 °C at one atmosphere pressure with N₂ as the carrier gas in a CVD reactor. The gas phase reaction is shown in Equation (11).



Ammonia carried by a stream of N₂ mixes in the hot zone with Me₃NAlH₃ carried on a stream of N₂. Films obtained under these conditions are uniform, transparent and adhere well to the substrate. The optical transparency of the films on quartz has been examined by UV-Vis. spectroscopy and the spectrum is shown (200nm - 800 nm) in Figure 15.

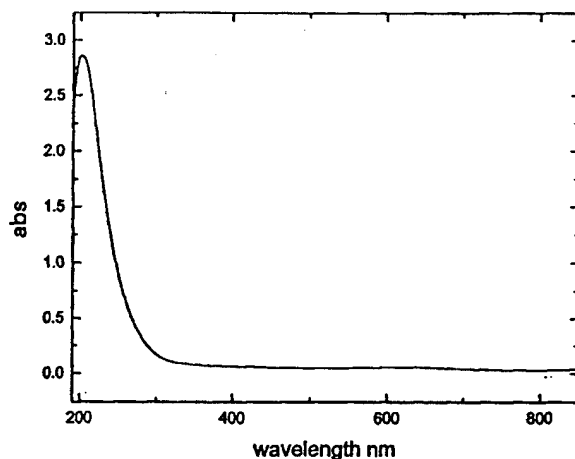


Figure 15. Optical transparency of AlN film on quartz.

The infrared spectrum from a film prepared at 500 °C and annealed at 600 °C for 24 hours was in excellent agreement with that of AlN powders, which we characterized by IR, XRD and solid state MAS ^{27}Al NMR spectroscopy. Figure 16 depicts SEM images of the surface and cross-section. In Figure 16a most of the crystallites depicted are less than $0.2\mu\text{m}$. In Figure 16b the thickness of the film is shown to be about $1\mu\text{m}$.



Figure 16a. AlN film.

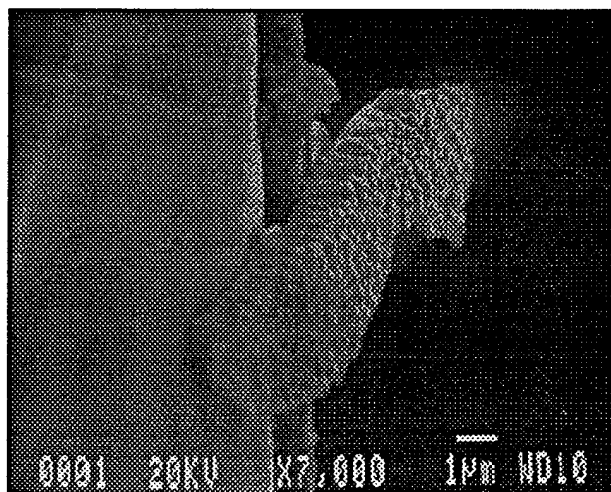
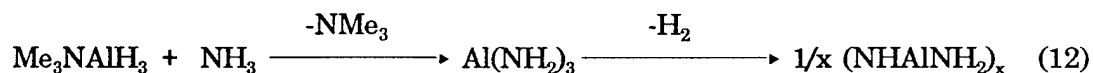


Figure 16b. Cross section of AlN film.

AlN powders were prepared by first allowing Me_3NAIH_3 carried on a stream of N_2 to react with NH_3 at room temperature (Equation (12)). The $(\text{H}_2\text{NAIH}_2)_x$ formed is a very finely



divided powder. Pyrolysis of this powder at 1000 °C produced AlN powder which was characterized by IR, XRD and solid state ^{27}Al NMR spectroscopy. The SEM image this powder shows crystallites that are consistently smaller than 0.2 μm .

XI. Publications, Patent, Dissertations

A. Publications

1. "Complexes of Divalent Lanthanides (Yb(II), Eu(II), Sm(II)) with Decaborates," J. P. White, III, S. G. Shore *Inorg. Chem.* **1992**, *31*, 2756.
2. "Preparation of Amorphous Boron Nitride and its Conversion to a Turbostratic, Tubular Form" E. J. M. Hamilton, S. E. Dolan, C. M. Mann, H. O. Colijn, C. A. McDonald, S. G. Shore *Science*, **1993**, *260*, 650.
3. "Synthesis and Structure of Triethylammonium 2-acetonitrile-nonahydro-closo-decaborate(-1)" D. Dou; I. J. Mavunkal; J. A. Krause Bauer; C. B. Knobler; M. F. Hawthorne; S. G. Shore *Inorg. Chem.* **1994**, *33*, 6432.
4. "Synthesis and Structure of Triphenylmethyl Phosphonium tetrakis-tetrahydroborato Aluminate, $[\text{Ph}_3\text{MeP}][\text{Al}(\text{BH}_4)_4]$, an Example of Eight Coordinate Aluminum(III)" D. Dou; J. L. Liu; J. A. K. Bauer; G. T. Jordan, IV, S. G. Shore *Inorg. Chem.* **1994**, *33*, 5443.
5. "Amorphous Boron Nitride Prepared from the Reaction of Haloborazines with Alkali Metals; Formation of a Novel Tubular Morphology by Thermal Annealing" E. J. M. Hamilton; S. E. Dolan, C. M. Mann; H. O. Colijn; S. G. Shore. *Chem. Materials.* **1995**, *7*, 111.
6. "Formation of $[\text{BH}_3]^{2-}$ and $[\text{B}_2\text{H}_6]^{2-}$ From the Homogeneous Reduction of B_2H_6 " R. A. Godfroid; T. G. Hill; T.P. Onak; S.G. Shore *J. Am. Chem. Soc.* **1994**, *116*, 12107.
7. "Charge Transfer Complexes of Decaborane(14) and 2,4-Diiododecaborane(14); The X-ray Crystal Structure of $[\text{P}(\text{C}_6\text{H}_5)_3\text{CH}_3][2,4\text{-I}_2\text{B}_{10}\text{H}_{12}]$ " J. R. Wermer; O. Hollander; J. C. Huffman; J. A. Krause Bauer; D. Dou; L.-Y. Hsu; D. L. Leussing; S. G. Shore *Inorg. Chem.* In press.
8. "Reactions of Aluminum Hydride Derivatives with Ammonia-Borane: A New Approach toward AlN and AlN/BN Materials" Danan Dou, Ewan J. M. Hamilton; Pierre A. Florian; Karl E. Vermillion; Philip J. Grandinetti; Sheldon G. Shore *Chem. Materials.* Submitted.

B. Patent

"Method for the Preparation of Boron Nitride Using Amine-Haloborane." United States Patent 5,169,613, December 8, 1992. S. G. Shore; Phillip Niedenzu, Allison DeGraffenreid,

C. Dissertations

1. "Preparation of Ytterbium and Europium Borides from Yb(II) and Eu(II) Boron Hydride Precursors" Terese A. Salupo, Ph. D. Dissertation The Ohio State University, 1993.

2. "Studies in the Reduction of BH_3 : Formation of the Borate Dianions $[\text{BH}_3]^{2-}$ and $[\text{B}_2\text{H}_6]^{2-}$; Preparation and NMR Studies of Rhodium(I) and Copper(I) Nonahydrohexaborate Complexes" Robert A. Godfroid, Ph. D. Dissertation The Ohio State University, 1994.

XII. Participating Scientific Personnel

Professor Sheldon G. Shore

Dr. Danan Dou

Dr. Ewan Hamilton

Dr. Terese Salupo (Ph. D. 1993)

Dr. Robert Godfroid (Ph. D. 1994)

XIII. Report of Inventions

There were no inventions during the grant period. For the patent issued during the grant period, the invention was made during the preceding grant and was duly noted in the final report. for Grant No. DAAL03-88-K-0176.

XIV. Bibliography

1. Godfroid, R. A.; Hill, T. G.; Onak, T. P.; Shore, S. G. *J. Am. Chem. Soc.* **1994**, *116*, 12107.
2. Stock, A.; Sutterlin, W.; Kurzen, F. *Z. Anorg. allgem. Chem.* **1935**, *225*, 225.
3. a) Klemm, L.; Klemm, W. *Z. Anorg. allgem. Chem.* **1935**, *225*, 258. b) Hough, W. V.; Edwards, L. J.; McElroy, A. D. *J. Am. Chem. Soc.* **1956**, *78*, 689. c) Hough, W. V.; Edwards, L. J.; McElroy, A. D. *J. Am. Chem. Soc.* **1956**, *80*, 1828. d) Hough, W. V.; Edwards, L. J. *Advances in Chemistry Series*, **1961**, *32*, 184. e) Hersmanek, S.; Plesek, J. *Collect. Czech. Chem. Commun.* **1966**, *31*, 177. f) Gaines, D. F.; Schaeffer, R.; Tebbe, F. *Inorg. Chem.* **1963**, *2*, 526. g) Hill, T. G.; Godfroid, R. A.; White, J. P., III; Shore, S. G. *Inorg. Chem.* **1991**, *30*, 2952. h) Burg, A. B.; Campbell, G. W. *J. Am. Chem. Soc.* **1952**, *74*, 3744. i) Campbell, G. W. *J. Am. Chem. Soc.* **1957**, *79*, 4023

4. Biffar, W.; Nöth, H.; Sedlak, D. *Organometallics*, **1983**, *2*, 579
5. Wegner, P. A.; Adams, D. M.; Callabretta, F. G.; Spada, L. T.; Unger, R. G. *J. Am. Chem. Soc.* **1973**, *22*, 7513.
6. Mustyatsa, V. N.; Votina, N. A.; Solntsev, K. A.; Kizemtspv. N. T. *Dokl. Chem. Proc. Sov. Acad. Sci. (Engl. Transl.)* **1988**, *301*, 245.
7. Kuznetsov, N. T.; Solntsev, K. A. *Chemistry of inorganic Hydrides*; Nauka Publ. Moscow, 1990; p. 5.
8. Mebel, A. M.; Charkin, O. P.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 463.
9. a) Schmitt, A. P.; Middaugh, R. L. *Inorg. Chem.* **1974**, *13*, 163. b) Hawthorne, M. F.; F. P. Olsen *J. Am. Chem. Soc.* **1965**, *87*, 2366; c) Miller, H. C.; Hertler, W. R.; Mueterties, E. L.; Knoth, W. H.; Miller, N. E. *Inorg. Chem.* **1965**, *4*, 1216.
10. Dou, D.; Mavunkal, I. J.; Krause Bauer, J. A.; Knobler, C. B.; Hawthorne, M. F.; Shore, S. G. *Inorg. Chem.* **1994**, *33*, 6432.
11. Wegner, P. A.; Adams, D. M.; Callabretta, F. G.; Spada, L. T.; Unger, R. G. *J. Am. Chem. Soc.* **1973**, *22*, 7513.
12. Wermer, J. R.; Hollander, O.; Huffman, J. C.; Krause Bauer, J. A.; Dou, D.; Hsu, L.-Y.; Leussing, D. L.; Shore, S. G. *Inorg. Chem.* submitted.
13. a) Titov, L. V.; Krasnoperova, V. D.; Rosolovskii, V. Ya. *Izv. Akad. Nauk SSSR. Ser. Khim.*, **1972**, *4*, 754. b) Titov, L. V.; Sansnovskaya, V. D.; Rosolovskii, V. Ya. *Izv. Akad. Nauk SSSR. Ser. Khim.*, **1974**, *11*, 2410. c) Titov, L. V.; Sansnovskaya, V. D.; Rosolovskii, V. Ya. *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1976**, *8*, 1689.
14. Dou, D.; Liu, J. P.; Bauer, J. A. K.; Jordan, G. T., IV; Shore, S. G. *Inorg. Chem.* **1994**, *33*, 5443.
15. Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73 and references therein.
16. a) Hamilton, E. J. M.; Dolan, S. E.; Mann, C. M.; Colijn, H. O.; McDonald, C. A.; Shore, S. G. *Science*, **1993**, *260*, 659. b) Hamilton, E. J. M.; Dolan, S. E.; Mann, C. M.; Colijn, H. O.; McDonald, C. A.; Shore, S. G. *Chem. Materials*. In press.
17. White, J. P., III; Deng, H.-B.; Shore, S. G. *Inorg. Chem.* **1992**, *31*, 2756. b) White, J. P., III; Deng, H.-B.; Shore, S. G. *J. Am. Chem. Soc.* **1989**, *111*, 8946.
18. White, J. P. III; Shore, S. G. *J. Am. Chem. Soc.* **1991**, *30*, 2337.
19. Iijima, S. *Nature* **1991**, *354*, 56.
20. Ugarte, D. *Nature* **1992**, *359*, 707.

21. a) Smith, D. J.; McCartney, M. R.; Tracz, E.; Borowiecki, T. *Ultramicroscopy* 1990, 34, 54.; b) Alstrup, I. *J. Catalysis* 1988, 109, 241 and references therein.
22. a). Twait D. J.; Lackey, W. J.; Smith, A. W.; Lee, W. Y.; Hanigofsky, J. A. *J. Am. Ceram. Soc.* 1990, 73(6), 1510. b) Lee, W.; Lackey, W. J.; Freeman, G. B.; Angrawal, P. K.; Twait, D. J. *J. Am. Ceram. Soc.* 1991, 74 (9), 2136; c) Lee, W. Y.; Lackey, W. J.; Angrawal, P. K.; Freeman, G. B. *J. Am. Ceram. Soc.* 1991, 74(10), 2649.
23. Morris, J. R. J.; Tanzilli, R. A. *US. Patent No.* 4666873.
24. Bolt, J. D. *US Patent No.* 4764489
25. Kwon, D.; Schmidt, W. R.; Interrante, L. V.; Marchetti, P.; Maciel, G. *Inorg. Organomet. Oligomers*, Proc. IUPAC Symp. Macromol., 33rd 1991, Eds. Harrod, J. F.; Laine, R. M., Kluwer, Dordrecht, Neth. pp. 191-7.
26. Dou, D.; Hamilton, J. M.; Florian, P.; Vermillion, K; Grandinetti, P; Shore, S. G. *Chem. Mater.* Submitted.
27. Yu, C.; Kim, S.; Meikle, S.; Doan, T. T.; Blalock, *Mat. Res. Soc. Symp. Proc.* 1992, 264, 461.
28. a) Sheppard L. M.; *Ceram. Bull.* 1990, 69, 1801. b) Neuberger, *Handbook of Electronic Materials* , 1971, Vol. 2,IFI/Plenum, New York, pp 18-20. (c) Yin, W. M.; Stofko, E. J.; Zanzucchi, P. J.; Ettenberg, M.; Gibert, S. L. *J. Appl. Phys.* 1973, 44, 292. (d) Slack, G. A.; *J. Phys. Chem. Solids* 1973, 34, 321
29. a) Fathimulla, A.; Lakhani, A. A.; *J. Appl. Phys.* 1983, 54, 4586. b) Interrante, L. V.; Lee, W.; McConnell, M.; Lewis, N.; Hall, E.; *J. Electrochem. Soc.* 1989, 136, 472.
30. a) Shiosaki, T.; Yamamoto, T.; Oda, T.; Kawabat, H.; *Appl. Phys. Lett.* 1980, 36, 643. b) Yoshida, S.; Misawa, S.; Fujii, Y.; Takada, S.; Hayakawa, H.; Gonda, S.; Itoh, A. *J. Voc. Sci. Technol.* 1979, 16, 990.