# Synthetic Routes to Boron Nitride

ROBERT T. PAINE* and CHAITANYA K. NARULA[†]

Department of Chemistry and Center for Microengineered Ceramics, University of New Mexico, Albuquerque, New Mexico 87131

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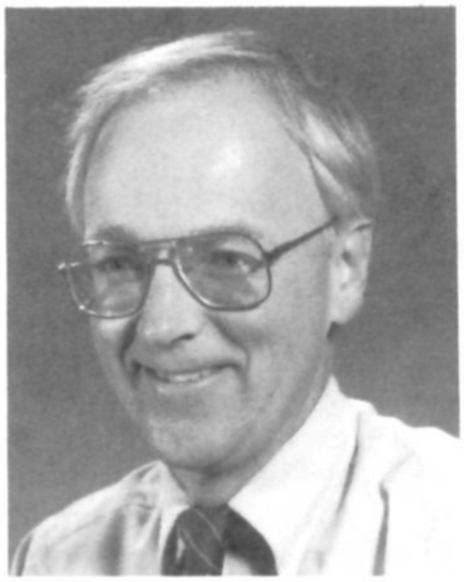
## Contents

## I. Introduction

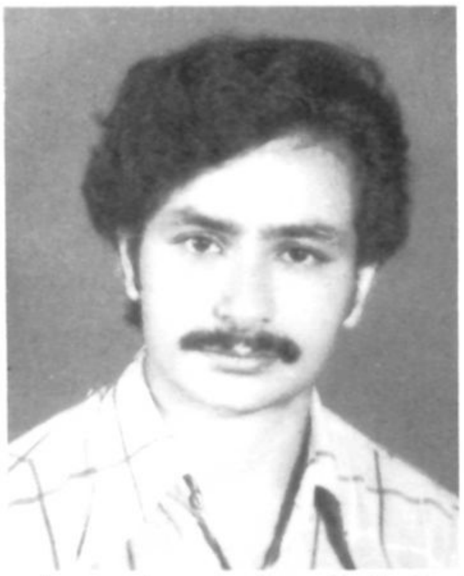
Until recently, whenever the word ceramics was used, chemists conjured up visions of white wares and firebrick. It is true that common inorganic oxides, e.g., silica, alumina, and magnesia, have long dominated ceramics science and engineering, and the fundamental understanding of their chemistry, powder processing, and physical properties is highly developed. Numerous commercial applications have been derived for oxide materials, and one might conclude that the ceramics field is mature and devoid of interesting problems for research chemists. In fact, this is far from an accurate conclusion for oxides or non-oxides. In succeeding sections, it will be illustrated that advanced ceramics are rich with exciting chemical problems and dependent upon chemistry for future development. This will be demonstrated by the chemistry and processing of one non-oxide ceramic, boron nitride.

Historically, the selection of a conventional ceramic for an application has usually been guided by a single, dominant performance characteristic, such as mechanical strength, thermal conductivity, electrical conductivity, or optical transmission. Limitations incurred by powder quality and processing chemistry have rarely played a central role in the selection process, and shortcomings have been "engineered around". In particular, single-function, traditional oxides have typically served in secondary or enabling roles in which they allow for improved performance or extended application ranges for a primary device or process. By operating in this mode, the ceramics industry has slowly grown from a cottage status to a position of worldwide commerical stature.

Although they are widely utilized today, conventional oxides fail to meet many current and future materials technology needs. Older, crude materials are being replaced in new, consumer, manufacturing, and defense products by advanced or high-performance materials with complex molecular compositions, fine microstructures, and precise performance characteristics. Like their simple predecessors, advanced ceramics serve in enabling roles; however, their unique compositions and



Robert T. Paine was born in Colorado Springs, CO, in 1944. He received his B.S. degree from the College of Chemistry, University of California, Berkeley (1966), and Ph.D. (with R. W. Parry) from the University of Michigan (1970). Following postdoctoral studies at Northwestern University (with F. Stafford) and Los Alamos National Laboratory (with L. B. Asprey), he joined the faculty at the University of New Mexico as an Assistant Professor in 1974. In 1983 he was appointed Professor of Chemistry. His current research interests are in the development of main-group precursors to solid-state materials, the design of metal-ion-specific organic extractants and immobilization of these extractants on solid supports and membranes, the formation of new main-group ring and cluster configurations, and the assessment of the reactivity of main-group metal carbene and carbyne analogues.



Chaitanya K. Narula was born in Etawah, India, in 1955. He received his M.Sc. from the University of Roorkee (1975) and Ph.D. from the University of Rajasthan (1980). He was a postdoctoral fellow at the University of Delaware (with R. F. Heck), a junior Alexander-von-Humboldt Fellow at the Universität München (with H. Nöth), and a postdoctoral fellow at the University of New Mexico (with R. T. Paine and R. Schaeffer). He is currently a Research Scientist in the Chemical and Physical Science Laboratory at Ford Motor Company, Dearborn, MI. His research interests include synthetic, structural, and computational aspects of unstable species in the chemistry of main-group elements, advanced materials derived from these elements, electrochromic effects in metal oxides, and chemical approaches to surface modification.

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[†] Present address: Ford Motor Co., Dearborn, MI.

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structural, electronic, and optical properties also allow them to operate in crucial primary capacities. They are being designed to simultaneously display several useful functions, and they are being organized in devices to accomplish increasingly complex, multiple characteristic tasks under extreme conditions. The rational design of such multifunction ceramics presents formidable and exciting experimental and theoretical challenges for a wide range of scientists and engineers. Chemistry is central to these challenges, and a host of fascinating chemical problems await attention. Timely and inventive chemical studies will ensure stunning technological advances and stimulate the voracious high-technology materials market.

Ceramics, defined as refractory, inorganic materials,[1] are not limited to oxide compounds. Non-oxide ceramics, such as borides, carbides, nitrides, and silicides, in one or more crystalline modifications, are known for their high mechanical strength, hardness, corrosion resistance, oxidation resistance, thermal shock stability, wide variation in electronic properties, and, unfortunately, their brittle character. These compounds have traditionally received less attention than oxide ceramics due, in part, to difficulties encountered in routinely obtaining pure materials with well-defined bulk properties, grain characteristics, and microstructures. However, the dramatically increased demand for rugged ceramics has led to greater interest in non-oxide materials, and their development is now a key element in the design of advanced ceramics and their composites.

One old commercially important non-oxide ceramic is boron nitride, BN. This deceptively simple material has enjoyed widespread use, particularly in a narrow range of traditional thermal/structural applications, but deficiencies in synthetic and processing methods have ultimately restricted its utilization in many advanced ceramic applications. Nonetheless, several unique bulk properties of BN have stimulated renewed interest in its chemistry and processing, and demands have appeared for fibers, coatings, and foams that cannot be obtained by classical high-temperature powder preparative methods.

In this review, we will confine attention to the synthesis, and to a lesser extent, the processing of boron nitride in its hexagonal modification, h-BN. The extensive preparative and processing literature on the cubic modification has not been included here. The traditional synthetic routes to h-BN and its properties were briefly reviewed by Archer[2] in 1977 and by Meller[3] in 1983 and 1988. In the present review, some aspects of these accounts will be retraced; however, the primary focus is on molecular and polymeric precursor chemistry and processing science developed in the past 10 years.

## *II. Selected Properties*

Boron nitride is isoelectronic with carbon, and like carbon, its properties are highly dependent on the crystalline modification under study.[4] Boron nitride is primarily found in a hexagonal h-BN ($\alpha$-BN) form that resembles graphite, sphalerite-type $\beta$-BN forms related to cubic diamond, and wurtzite-type $\gamma$-BN forms related to hexagonal diamond. For the fully ordered graphitic modifications, the lattice constants for boron nitride and carbon are similar: BN, $a = 2.504$ Å, $c = 6.661$ Å; C, $a = 2.456$ Å, $c = 6.696$ Å. Although the structure of h-BN is analogous to the graphitic form of carbon, with strong bonding within the atomic layers and weak bonding between layers, the h-BN structure differs, as shown in Figure 1, by having the planar, fused, six-membered rings stacked directly on top of each other, with boron atoms in one layer serving as nearest neighbors to N atoms in adjacent layers. In the graphitic carbon structure, the carbon atoms in adjacent layers are offset. The diamond-like modifications are metastable under standard conditions, and at this time, they are not obtained except under severe high-temperature, high-pressure conditions[3] or by shock compaction.[5] Ion-assisted vapor deposition[6,7] and related energetic techniques[8] have also been reported to produce cubic BN or close relatives typically designated as i-BN (i refers to ion-enhanced processing).[9] Once formed, diamond-like BN is kinetically stable in a fashion similar to diamond. It is very important to note that, under typical laboratory synthetic conditions (metallurgical, CVD, or polymer pyrolysis), amorphous BN is often obtained along with turbostratic or mesographitic modifications that possess disorder in the layered, hexagonal, graphite-like structure.[10,11] In some cases, these disordered materials can be converted to highly ordered h-BN by proper thermal annealing.[3] Fully ordered h-BN is only obtained with careful attention to processing details that seem to vary with each synthetic approach. Since some crucial properties are dependent on crystallinity, it is important to recognize and assess the degree of ordering, as indicated by X-ray powder patterns. Two illustrative XRD patterns are shown in Figure 2.

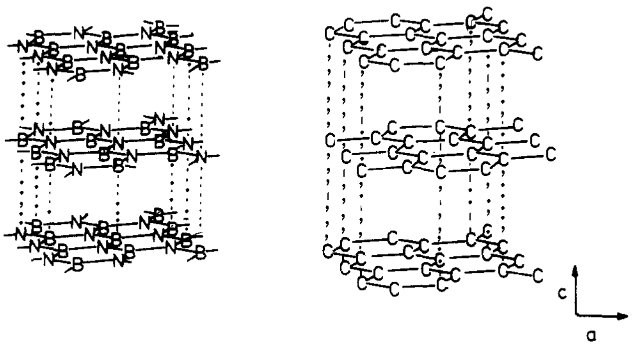


**Figure** 1. Comparison of graphite structures for BN and C. The lattice spacing, $c/2$, is 3.33 Å for BN and 3.35 Å for C.

It will be described in subsequent sections that most commercial boron nitride articles are prepared by hot pressing BN powders obtained from classical metallurgical high-temperature syntheses, e.g., boric acid and urea at 1000 °C, or by chemical vapor deposition (CVD) growth. The former material, when heat molded, is referred to as hot-pressed BN, and the latter material is called pyrolytic BN. The physical and chemical properties of these materials are often different, and because of the absence of binders and improved crystallinity and grain features in pyrolytic BN, the properties determined from this material are usually considered more representative. Consequently, specific properties discussed here are for pyrolytic BN unless stated otherwise.[2,3,12-14]

In powder or compacted forms, boron nitride has a silky feel, monoliths may be readily machined, and the material is nontoxic. Unlike graphite, which is characteristically black, h-BN, when pure and defect free,

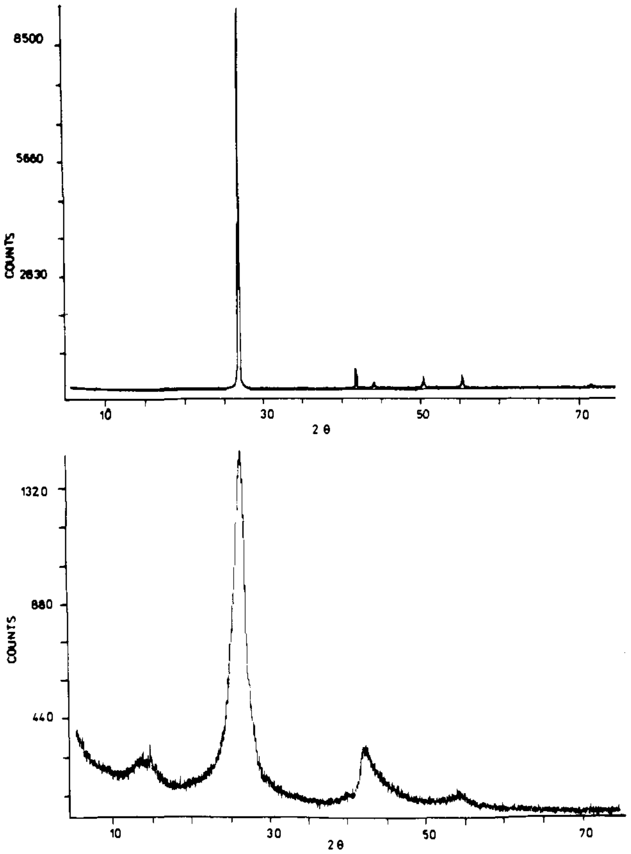


**Figure 2.** Illustrative X-ray powder diffraction patterns for boron nitride samples. (Top) highly ordered h-BN with lines indexed from left to right as (002), (100), (101), (102), (004), and (103). This corresponds to type D boron nitride, as described in ref 10. (Bottom) partially ordered boron nitride. This corresponds to type B in ref 10. Type A shows no resolution of the (100),(101) doublet or the less intense peaks at higher 2$\theta$.

is transparent. The opaque, white color typically found in macroscopic samples is not intrinsic, but rather it results from impurity and defect states in the electronic band gap.[15] Indeed, thin sections of pyrolytic BN are reported to be translucent, and some samples of white BN may be converted to the translucent state by application of pressure. The density of anisotropic pyrolytic BN may be as low as 2.0 g cm$^{-3}$, while the theoretical density[11] is 2.27 g cm$^{-3}$. This density is the lowest of the ceramic materials. Low-density (<2.0 g cm$^{-3}$) isotropic and anisotropic samples may be thermally annealed to improve the density. Unlike graphite, pyrolytic BN does not appear to recrystallize at high temperatures under tensile deformation parallel to the basal planes.[16] However, related to the point made above, at 2300–2400 °C, compressive annealing perpendicular to the basal planes is reported to result in densification and recrystallization.[17] The resulting material is soft, flaky, transparent, and highly reflective.

Boron nitride apparently does not display a normal melting behavior; however, it is reported to sublime under an atmosphere of nitrogen at 2330 °C.[2] The material displays a dissociation pressure of 1.8 × 10$^{-2}$ Torr at 1900 °C and 4.3 Torr at 2300 °C. Melting would be expected to occur under high pressures, and an estimate of this property would be useful to those engaged in materials component design.

As mentioned above, the layered structures of BN and graphite, with very strong in-plane covalent bonding and weak interplane attractions, are unique in ceramic materials, and this feature results in a number of quite anisotropic mechanical, thermal, and electrical properties. For example, pyrolytic BN has a high compressive strength, 30 000 psi (25 °C) in the *c* direction, while the bend strength (15 000 psi (25 °C)), tensile strength (6000 psi (25 °C)), and Young's modulus (3 × 10$^6$ psi (25 °C)) are higher in the *a* direction.[18] The Poisson ratio in the *a* direction is 0.025 (25 °C). Pyrolytic BN has excellent thermal shock resistance in the temperature region 2000 to 25 °C, and it has a specific heat of 0.24 cal g$^{-1}$ °C$^{-1}$, which is comparable to that of magnesium and aluminum. Like graphite,[12] the thermal expansion and thermal conductivity are highly anisotropic. The thermal expansion for BN is low in the *a* direction parallel to the surface, 5 × 10$^{-4}$ mm/mm (250 °C) and 1.7 × 10$^{-3}$ mm/mm (1100 °C), and comparatively large in the *c* direction normal to the planes, 4 × 10$^{-2}$ mm/mm (1100 °C). The thermal conductivity, on the other hand, is large in the *a* direction, 0.15 cal s$^{-1}$ cm$^{-2}$ °C$^{-1}$ cm$^{-1}$ (25–800 °C), and smaller in the *c* direction, 0.0035 cal s$^{-1}$ cm$^{-2}$ °C$^{-1}$ cm$^{-1}$ (25 °C) and 0.007 cal s$^{-1}$ cm$^{-2}$ °C$^{-1}$ cm$^{-1}$ (800 °C). It should be noted that the distinct anisotropic thermal properties of BN are responsible for its widespread use in fabrication of high-temperature crucibles. Thermodynamic data for h-BN have been summarized:[3] $C_p$(298 K) = 4.173 cal mol$^{-1}$ K$^{-1}$, $H°_{298} - H°$ = 628 cal mol$^{-1}$, $S°_{298}$ = 3.536 cal mol$^{-1}$ K$^{-1}$, $\Delta H$(298 K) = −60.38 kcal mol$^{-1}$, $\Delta H_{at}$(298 K) = 307.6 kcal mol$^{-1}$. For the reader interested in extended comparisons with carbon, mechanical and thermal data for graphite are summarized by Lozier and Manofsky.[19]

The electrical properties of BN and graphite are distinctly different. As mentioned above, graphite is a black, highly reflective semimetal with anisotropic resistivity: (0.4–5) × 10$^{-4}$ Ω cm in the *a* direction and 0.2–1.0 Ω cm in the *c* direction.[19] The resistivity of BN is much smaller at lower temperatures, making the material a useful insulator:[18] resistivity in the *a* direction, 3 × 10$^7$ Ω cm (1000 °C); resistivity in the *c* direction, 3 × 10$^9$ Ω cm. The dielectric constant for BN at 25 °C is 5.12 in the *a* direction and 3.49 in the *c* direction, and the dielectric strength is 2 × 10$^6$ V mm$^{-1}$ (25 °C). As expected, these electrical properties are highly dependent on purity, and resistivity may be influenced by sample annealing in nitrogen.[20] At higher temperatures, the resistivity decreases (e.g., at 1500 °C, 6 × 10$^3$ Ω cm (*a* direction) and 3 × 10$^5$ Ω cm (*c* direction)), and the material eventually becomes a semiconductor. This has adversely impacted design plans in potential reentry vehicle applications; however, it may be possible to realize some useful properties from the semiconducting properties for other high-temperature, extreme environment applications. Additional specialized electrical characteristics are summarized in the *Gmelin* reviews.[3]

There has been considerable debate over measured and calculated values of the band gap;[3] however, a value of 5.2 eV ($\pi$ band) appears to be sound.[15] Optical absorption and emission properties of h-BN have been studied extensively, and key data are concisely summarized.[3] Infrared spectra have been studied by Miller,[21] Margrave,[22] and Li[23] and found to be simple and diagnostic, yet dependent upon the degree of purity and crystallinity. Metallurgically prepared h-BN, for

**Figure 3.** Infrard spectra for h-BN. (Top) highly ordered BN. (Middle) polyborazinylamine pyrolysis product formed in a nitrogen atmosphere at 900 °C and briefly fired at 1200 °C in air. The weak band at ~3200 cm$^{-1}$ corresponds to a BOH band due to partial oxidation. (Bottom) polyborazinylamine pyrolysis product formed in an ammonia atmosphere at 1200 °C. The peak at ~3480 cm$^{-1}$ indicates residual N-H groups.

example, shows a strong, broad absorption centered at ~1370 cm$^{-1}$ and a sharp, weak band at ~810 cm$^{-1}$. Pyrolytic BN, on the other band, shows bands centered at ~1310 and 810 cm$^{-1}$, and the presence of residual N-H bonds is revealed by an absorption at ~3500–3200 cm$^{-1}$. Three typical spectra are shown in Figure 3. The Raman spectra of boron nitride samples are also useful for the characterization of h-BN and for the detection of carbon impurities. Detailed infrared and Raman spectroscopic studies and normal mode analyses were reported by Geick and co-workers.[24] Point defects in h-BN induced by ionizing radiation have been thoroughly studied, and an analysis of this work has been given by Katzir and co-workers.[25]

Knowledge of the chemical reactivity of ceramic materials is of crucial importance in determining the suitability of a particular material for an application. The reactivity of h-BN has been studied extensively; however, in many cases the samples employed were of unknown quality. This is especially true of oxidation studies where reports on the oxidation onset temperature range from 600 to 1200 °C. It is clear that this chemistry is very dependent on BN sample preparation, purity, crystallinity, and microstructure. Relatively recent work has taken care to describe some of the physical properties of BN used in reactivity studies and some trends have emerged. For example, it appears that, for pyrolytic BN, air oxidation (as measured by weight loss due to volatilization of $B_2O_3$) is negligible below 900 °C. However, oxidation becomes significant in the range 1100–1200 °C (4.8 mg cm$^{-2}$ in 180 min at 1200 °C).[26] Metallurgically prepared BN shows slight oxidation below 950 °C and more extensive weight loss at 1000 °C.[26] Commercial pyrolytic BN also has been reported to undergo weight loss due to oxidation on a 1-cm$^2$ surface exposed to an air flow of 1 ft/s at the following rates: $1 \times 10^{-4}$ g/min at 1400 °C and $1 \times 10^{-2}$ g/min at 2000 °C.[18] Calcining powdered BN in air, on the other hand, shows significant formation of $B_2O_3$ at 800 °C.[27] Of importance in coating technology, BN is reported to react with $Al_2O_3$ at 1700 °C and SiC at 800 °C.[28] A number of studies of reactions between BN and metals, alloys, and metal nitrides have appeared.[3] Several recent studies of intercalation chemistry with h-BN have appeared,[29-33] and this appears to be a very fruitful and fascinating area for additional work.

## *III. Selected Applications*

Although h-BN has not attracted the attention given to SiC and $Si_3N_4$, it nonetheless has been used in a diverse collection of device- or process-enabling applications that take advantage of its high-temperature shock stability, anisotropic thermal conductivity, electrical resistivity, and mechanical properties. A comprehensive list of uses has been given,[3] and the reader is referred to those reviews for many additional specific literature citations. Only a few highlights are listed here as illustrations.

Perhaps the largest volume application for powdered h-BN involves its use in high-temperature crucibles and evaporator boats that are employed in the semiconductor industry for containing Si and GaAs melts.[3,34] The powders also find a large-volume application as the raw material for the high-temperature, high-pressure conversion of h-BN to c-BN. The thermal conductivity and lack of wetting by many metals have led to applications of boron nitride in horizontal casters in the steel industry,[35] mold-release agents for castings, casting nozzles, binders or fillers for organic polymers and resins, and insulation material for power transformers.[3] The high-temperature lubrication properties of h-BN have provided uses in abrasive tools, liquid-metal processing, and motor oil compositions. The electrical properties have resulted in applications as electrode materials, electrode coatings, and semiconductor heat sinks. Boron nitride is noted to be partially transparent to infrared and microwave radiation, and the material has found some use as radar and infrared windows. There are some limitations, however, as a result of the intrinsic cutoff limit at short wavelengths and scattering resulting from sample anisotropy. Some CVD-prepared materials may allow for reduction of the latter problem. Pyrolytic films are used in a number of applications where metallurgical powders or hot-pressed powders are inadequate. These include the formation of anticorrosive layers, oxidation-resistant coatings, humidity-sensing devices, X-ray lithography masks, and as a semiconductor packaging and dielectric material.

In the past few years, h-BN has found increasing attention in advanced ceramic composite applications. Rice[36-38] has written several timely general reviews addressing aspects of toughening ceramic matrix composites, refractory ceramic fiber composites, and ceramic fiber coatings. These articles point out the need for designed multicomponent materials, and it is clear that boron nitride will play an important role in some complex materials. Some progress, not mentioned in the following preparative chemistry sections (sections IV–VII), has been made in forming composites with BN powder additives, fibers, coatings, binders, and matrix materials, and an outline of some recent advances is given here as an indicator of the importance that molecular and polymer precursor chemistry may play in the future.

Many aerospace applications require materials that can withstand high temperatures and repetitive thermal shock conditions. Although many ceramics are capable of surviving high-temperature environments, most are intrinsically prone to brittle failure under stress. Rossi[39,40] analyzed the fundamental problems in thermal shock and crack nucleation and propagation; and he concluded that thermal shock resistance could be improved by reduction of the elastic modulus of the ceramic. For the intended applications, it was also concluded that this might be best accomplished by fabrication of composites with proper control of the ratio of inclusion modulus to matrix modulus and the shape of the included phase. Experimentally, metal carbide–graphite and metal oxide (BeO, $Al_2O_3$)–BN composites were prepared, and the graphite and BN flake (75–350 μm) inclusions in the ceramic matrices were found to provide a high density of flaws that controlled crack propagation. As a result, these materials showed promise for specific thermal shock resistant applications.

In a similar vein, Rice and co-workers[41,42] further analyzed thermal shock resistance, ablation, and dielectric properties for $Al_2O_3$–BN and mullite–BN composites in which small (1–10 μm) BN platelets were employed. The hot-pressed ceramic composites retained good mechanical strength and superior thermal shock behavior, but they also developed a high degree of sample anisotropy due to alignment of the BN flakes during hot pressing. In an effort to reduce anisotropy, Coblenz and Lewis[43] produced BN in situ in $Al_2O_3$ and mullite matrices by reaction of a metal nitride, e.g., AlN or $Si_3N_4$ and $B_2O_3$. The mechanical properties were found to be intermediate between the extremes of anisotropic samples, and it was suggested that further improvements might be obtained by more controlled dispersion of the BN particles.

In an effort to improve the electrical properties of hot-pressed BN in wet environments, Murato and Miccioli[44] prepared BN/$SiO_2$ composites, and they noted effects on dielectric and thermal properties for a 40% BN sample. They found that the *c* axis of the BN crystals oriented parallel to the hot-pressing direction, and this orientation was enhanced by $SiO_2$ addition. The thermal expansion coefficient and thermal conductivity decreased in the composite, and the anisotropy in the expansion decreased. Stable, low-loss dielectric properties were also obtained.

There has been interest in obtaining BN fibers as an alternative to flakes for arresting brittle failure of ceramic–ceramic and metal–ceramic composites. Economy and co-workers[45–48] reported the formation of fibers by nitriding $B_2O_3$ filament, and critical processing factors including filament diameter, degree of nitriding, and conditions for hot stretching have been given.[48] Lindemanis[49] has described more recent studies of the same system, but it is not clear if these fibers have found practical use in composite forms or if their crack-arresting properties in brittle matrices have been tested.

Of course, there has been a great deal of interest in reducing failure of brittle matrices by incorporation of several other well-known fibers, e.g., graphite, SiC, and $Si_3N_4$. Unfortunately, in some matrices these fibers bond strongly with the matrix, and the strength of the composite is not significantly improved over the strength of the pure matrix. To offset bonding problems, fibers have been coated with another ceramic. For example, graphite coatings on SiC fibers reduce the bonding interaction between SiC and a metal matrix. This serves to improve crack deflection and fiber pull out characteristics. Unfortunately, the graphite coating tends to burn out when the composite is heated to high temperatures in air.

It has been suggested that BN coatings on fibers might offer an alternative approach to carbon coatings over a limited temperature range. Kazakov[50] reported the impregnation of oriented carbon with a solution of poly(arylacetylene) and carborane. It was claimed that pyrolysis of the mixture at 1500 °C produced a graphite with increased oxidation stability due to the formation of BN. Heating the mixture above 1500 °C produced lower stability. Expanding on the composites formed with BN flakes, Rice[51] described the use of CVD-deposited BN on SiC fibers in a silica matrix. The resulting composite showed a fourfold increase in strength and a large increase in fracture toughness over a composite without BN coating the SiC fibers. Freeman and co-workers[52] coated Nextel 312 fibers with BN by employing the CVD systems $BCl_3 + NH_3$ and borazene. The borazene CVD films provided better coatings, and the composites showed reduced fiber–matrix interactions and enhanced crack deflection.

Singh and Brun[53–55] recently reported a thorough study of CVD BN coated Nextel 440, SiC and carbon fibers incorporated into a hot-pressed mullite matrix. They noted that interfacial shear stress was reduced by the BN coatings, and the coatings clearly improved the fracture characteristics of the composite. Ruh and co-workers[56] have studied the phase characteristics of SiC–BN, and that work may have an important impact on future composite studies. For example, c-BN and c-SiC are soluble, and the boron nitride stabilizes the cubic SiC phase. SiC is not soluble in h-BN, and its Young's modulus decreases nonlinearly with increasing BN content.

A number of studies of BN–$Si_3N_4$ composites have appeared. Mazdiyasni and Ruh[57] studied the incorporation of h-BN powder in $Si_3N_4$ + 6% $CeO_2$ at 1750 °C. The BN remained as a discrete phase, and Young's modulus was decreased for the composite with introduction of BN. The dielectric constant of the composite was reduced by BN, and its thermal stress resistance was improved. Iwasa and Kakiuchi[58] reported a similar study, and they comment on a reduced Vicker's hardness for $Si_3N_4$ containing BN. They also mention that solid lubrication by BN is effective if the BN is adequately distributed.

Since $Si_3N_4$–BN hot-pressed articles have high thermal shock resistivity, there has been some interest in preparing coatings of $Si_3N_4$–BN by CVD techniques. Hirai[59] has reported attempts to prepare $Si_3N_4$–BN composites by vapor deposition. The films contained amorphous $Si_3N_4$ and turbostratic BN. In this condition, the films are probably not useful in protective or tribological applications. Besmann[60] has subsequently modeled the CVD process in an effort to better define optimum deposition conditions. Sugiyama and Ohsawa[61] report infiltration of $Si_3N_4$ preforms with BN by pulse CVI, and this technique may enjoy some interesting modifications and growth.

There have been few studies of the composite system AlN–BN. Mazdiyasni and co-workers[62] formed composites by hot pressing the respective powders, but BN (5–30%) remained as a discrete phase. No significant modification of the thermal expansion characteristics of AlN were found, and flexual strengths were lowered for samples with a $Y_2O_3$ sintering aid, particularly when measured at room temperature. Young's modulus also decreased with increasing BN content. Further reports by Kuramoto and co-workers[63] and Morris and Tangilli[64] in the patent literature describe attempts to prepare AlN–BN composites. The latter outlines applications of the composite in electromagnetic windows.

During the course of the manuscript review, it was brought to our attention that a review by Rice containing a thorough discussion of composites containing boron nitride is in press,[65] and we encourage the interested reader to consult that chapter when it is available. We maintain that the BN composite studies published to date establish this area as one deserving further attention. The materials hold promise not only for production of useful finished composite products, but they also offer a chance to study a variety of fundamental chemical effects in multicomponent ceramic systems.

The summaries provided in sections II and III are intended to illustrate the fascinating properties and applications of h-BN. In the following sections, we outline the wide array of synthetic approaches that have been used to prepare h-BN, with particular emphasis on recent developments in molecular and polymeric precursors that permit much greater flexibility in the formation if fibers, coatings, low-density materials, and composites.

## *IV. Classical High-Temperature Routes*

Until recently, the primary application for h-BN was for the construction of high-temperature crucibles and other pressure-sintered parts. These articles were prepared from powder samples by using classical hot-pressing techniques with or without sintering aids. Although not true in all cases, it was apparently not necessary for many of the older, high-volume applications to give a lot of attention to fine aspects of powder quality (e.g., purity, grain size homogeneity, and crystal lattice ordering); therefore, a wide variety of inexpensive boron and nitrogen reagents have been used to prepare h-BN. That chemistry has been thoroughly reviewed in the *Gmelin* series,[3,66] and papers by Archer,[2] Kalyoncu,[13] Fister,[67] and Rusanova[68] provide additional brief summaries of classical high-temperature syntheses. Some representative reactants and conditions include boric oxide or sodium borates and $NH_3$ (>900 °C, $NH_3$ or $N_2$), orthoboric acid or boric oxide and urea, biuret, guanidine, cyanamide, dicyanamide, thiourea, or melamine (>900 °C, $NH_3$), boron and nitrogen (>1200 °C), carbothermal reductions (e.g., boric acid and C (>1500 °C, $N_2$)), metal borides and $NH_3$ or $N_2$ (>1500 °C, $N_2$), and metal borohydrides and $NH_4Cl$ (>900 °C, $N_2$). The predominant commercial method for h-BN production today is carbothermic reduction. These syntheses are well grounded on high-temperature synthesis principles; e.g., the reactions are driven by the thermodynamic stability of h-BN, the gas-forming properties of the undesired C and O elements, and the reducing atmospheres. Further, silica has been added in some syntheses to getter sodium ions. Boric oxide, together with a second oxide, e.g., MgO and CaO, may be added in excess in some preparations to improve the subsequent hot-pressing characteristics of h-BN powder. The purpose of the second oxide is to reduce the volatility of $B_2O_3$ in the hot-pressing operation. All of the reactions proceed with good yields; they are simple and may be accomplished in batch or continuous modes.

Increasing engineering demands on advanced ceramic articles have forced powder producers to dramatically improve the characteristics of their products. The purity, grain size and shape, and crystallinity of h-BN formed in traditional high-temperature syntheses fluctuate considerably, and the variations are responsible for the differences in physical properties mentioned in section II. The variations are also responsible for irreproducible powder sintering behavior, unreliable mechanical properties, and variable oxidation stability of finished products. Fister[67] noted that, for advanced ceramic applications, the commercial powder producer must give attention to stringent specifications on grain size distribution, purity, grain shape, bulk properties, sinterability, workability, and price. Further, the producer is increasingly forced to tailor powders to very specific applications. He points out that, under a given set of conditions, a synthesis may produce coarse BN powder with good thermal conductivity but poor sinterability and high orientation in hot-pressed articles. These coarse particles are good for high-temperature lubrication applications. On the other hand, "fine" BN particles with irregular shapes and a high crystallite dislocation density may be produced under another set of conditions. These powders may be ideal for sintering, and the presence of boron oxides from the synthesis, together with MgO or CaO, improves the hot-pressing behavior.

Many reexaminations of high-temperature reactions have been initiated in the past few years, and a large number of reports appear in patents. For example, several reports have appeared on *purification* of h-BN by introduction of carbonaceous material during a final high-temperature, inert, or reducing-atmosphere pyrolysis step. This treatment presumably removes remaining oxide impurities.[69,70] Unfortunately, the influence of this treatment on physical properties for the powders or subsequently formed hot-pressed articles has not been described in any detail in the open literature. Alternative purifications calling for sample heating and cooling under $N_2$ gas have also been described.[71–75] The classic reactions of boric acid and metal borates with urea, melamine, cyanamide, and other N(H)-bearing compounds reported by King[76] and O'Connor[77] have been reexamined in more detail,[78–83] and it appears that these syntheses are popular for commercial manufacture of h-BN destined for refractory, electronic materials and lubricant applications.[80] Again, few systematic studies of synthesis and processing parameter influences on physical properties have appeared, and systematic studies of this type are needed.

The reaction of $Na_2B_4O_7$ and $NH_4Cl$ has been reexamined,[84] but it is not clear that this combination offers improvements over other related descriptions. A laboratory-scale synthesis utilizing combinations of $NaBH_4$ and $NH_4Cl$ has been reported.[13] In related chemistry, a claim for the formation of oxygen-free h-BN from the reaction of $KBH_4$ and $NH_4Cl$ (ratio N/B = 1.5) has been made with pyrolysis under nitrogen and heating in stages at a rate of 300 °C/h and final processing at 1050 °C.[85] Further, there have been reports of powder production from microwave discharge of $BCl_3$–$H_2$–$N_2$,[86] laser irradiation of $BF_3$, $BCl_3$, or $B(CH_3)_3$ and $NF_3$ or $N_2F_4$ mixtures,[87] thermolysis of $B_2O_3$ and $NH_3$ in a $Ca_3(PO_4)_2$ matrix,[88] pyrolysis of $BPO_4$ in combination with NaCN,[89] and pyrolysis of $BCl_3$, $NH_4Cl$, and $NH_3$ mixtures.[90]

The general impression gained from recent patent literature is that improved powder preparations and hot-pressing methods have resulted in production of articles with more reliable high-temperature stability and mechanical properties.[67] Still, it is apparent that alternative approaches are in great demand not only for the production of "fine" h-BN powders but also for high-quality ceramic forms such as fibers, films, and foams that are not accessible from powder synthesis techniques.

## *V. Vapor Deposition Routes*

Most alternative preparations of advanced ceramic materials have utilized vapor deposition techniques, including conventional chemical vapor deposition (CVD), metal organic chemical vapor deposition (MOCVD), low-pressure chemical vapor deposition (LPCVD), plasma-assisted (or plasma-enhanced) chemical vapor deposition (PACVD), laser-assisted chemical vapor deposition (LCVD), sputter processes, and ion-assisted processes. In most of these approaches, volatile precursors containing the final elements of interest (e.g., B and N) are passed over a substrate and a ceramic is deposited as an amorphous or crystalline thin film or fine powder, depending on the conditions employed. The advantages and disadvantages of these approaches as synthetic tools have been detailed in many places.[12,91-93] Specifically, for BN production, there are a limited number of precursors available that are both nonhazardous and free of sources of deleterious impurities. The topic of BN thin-film production has recently been thoroughly reviewed by Arya and D'Amico.[93] Only a brief summary and representative set of references for this subject are provided here.

The chemical combinations that have been most commonly employed in vapor deposition production of amorphous and crystalline (pyrolytic) BN powders and films include $B_2H_6/NH_3$, $B_2H_6/NH_3/H_2$, $BF_3/NH_3$, $BCl_3/NH_3$, $BCl_3/NH_3/H_2$, borazene ($H_3B_3N_3H_3$), trichloroborazene ($Cl_3B_3N_3H_3$), and $B_{10}H_{14}/NH_3$. These mixtures have been used to deposit films on a wide range of substrates including transition metals, structural ceramics, electronic ceramics, and glasses. As expected, the advantages of CVD methods are that the BN is uniformly deposited over regular and irregular shapes, it is formed at high deposition rates, and there is a good deal of control over morphology, crystal structure, and orientation.[93]

Of the mixtures listed above, $BCl_3/NH_3$ and $BCl_3/NH_3/H_2$ are probably the most widely employed.[93-100] A wide range of substrate deposition temperatures, 200–1300 °C, has been used, and films formed below 500 °C appear to be relatively unstable, while films produced below 650 °C are often amorphous. High-quality films are routinely formed above 1000 °C. Diborane–$NH_3$ and $B_2H_6$–$NH_3$–$H_2$ mixtures are also popular,[101-110] although the inherent atmospheric instability of diborane tends to hinder its application. Deposition temperatures have ranged from 300 to 1200 °C, with amorphous films obtained at lower temperatures and crystalline highly oriented films formed at higher temperatures.

Although expensive and relatively unstable, borazene ($(HBNH)_3$) and its derivatives have also gained some favor as vapor deposition sources for BN. Since borazene is a key component in syntheses described in the following sections, some additional details of the gas-phase deposition chemistry are provided. Adams[111] studied the decomposition of $(HBNH)_3$ under low-pressure CVD conditions on Si substrates at 300–650 °C, and he compared the properties of these films with those obtained from the CVD of $B_2H_6/NH_3$ mixtures at similar substrate temperatures. Borazene depositions at temperatures below 500 °C gave films with properties very different from films formed from $B_2H_6/NH_3$. Given infrared data and observations on the chemical reactivity of the films formed from borazene, it can be concluded that boron nitride was not formed at low temperatures. At higher temperatures, the films from the two chemical feedstocks are spectroscopically similar. Nonetheless, it is not at all obvious that the films obtained from borazene decomposition contain crystalline h-BN. Savel'ev and co-workers[112] studied the plasma-assisted vapor deposition of $(HBNH)_3$, and they claim that BN films are produced. Shanfield and Wolfson[113] have used $(HBNH)_3$ as the chemical source for ion-assisted vapor depositions, and they report formation of c-BN films. In another variation, Hoshino and Takase[114] report deposition of hexagonal and/or cubic BN from borazene with PACVD conditions under application of an electric field. They also claim film deposition rates 2–3 times faster than with $BCl_3/NH_3$. The borazene decomposition chemistry is very interesting from a chemical standpoint, and assessments of reproducibility and determinations of the mechanism of decomposition would be appropriate.

A few other less popular chemical systems have been reported for BN production. Constant and Feurer[115] have used hexachloroborazene ($Cl_3B_3N_3Cl_3$) alone as a CVD source for forming amorphous BN coatings at 900 °C. More recently, Schleich and co-workers[116] reported BN depositions employing MOCVD precursors, $(C_2H_5)_3N{\cdot}BH_3$ and $(C_2H_5)_2N(H){\cdot}BH_3$. The advantage of using these well-known adducts is that they permit use of the readily cleaved B–H bonds without the need for handling hazardous diborane(6). Related MOCVD precursors are, of course, routinely used to produce other III–V materials. Organoamine boranes, $R_3N\cdot BH_3$, have probably been avoided in the past as BN chemical sources due to the ever present potential for forming boron carbides. In addition, it is clear that there is some difficulty in maintaining sufficient nitrogen in the product films, and it is not apparent that the films have any degree of crystallinity. The system $B_{10}H_{14}/NH_3$ has been reported to form both boron-rich and stoichiometric BN films at a substrate temperature of 850 °C,[117] and the system $B_2H_6/C_2H_6/N_2$ has been noted to give B–C–N–H films.[118]

Vapor deposition techniques, like classical high-temperature methods, produce boron nitride powders and films with a wide range of physical characteristics. Furthermore, the large array of deposition variables provide both advantages and disadvantages, and it is difficult to compare properties of samples prepared by different investigators using different techniques. What has been correlated is summarized by Arya and D'Amico.[93] For example, product chemical composition depends greatly on the deposition technique, the chemical feedstock composition, and the substrate temperature. For example, films prepared by rf sputtering in Ar have an excess of boron, and $B_2H_6/NH_3$ CVD mixtures have a tendency to deposit mixtures of B in BN. Laser-assisted depositions have tended to produce so-called borohydronitride (B–H–N) films. Ion-assisted depositions typically contain oxygen and/or $B_2O_3$, and the presence of $B_2O_3$ from any deposition method degrades the chemical stability of the powder or film.

The adherence of BN films and their hardness appear to be relatively independent of deposition technique; however, film stress is highly dependent upon deposition methods and conditions. The thermal stability of films depends upon the final film purity, crystallinity, and deposition substrate temperature. Unfortunately, in this key area a systematic study has not been performed in one laboratory, so it is difficult to conclude precisely how oxidation and thermal stability vary as a function of crystallinity and/or substrate temperature. Optical properties seem to be highly variable in magnitude as a function of deposition conditions. Lastly, it is pointed out that the various ion-assisted vapor deposition techniques produce i-BN films that are reportedly very hard. These films are attracting commercial attention despite their tendency to be substoichiometric, to retain significant amounts of impurities, and, in some cases, to have elevated reactivities compared to traditional h-BN powders.

The crystallinity of vapor-deposited films depends greatly on deposition conditions. Many of the films and powders are amorphous; however, with proper care, vapor deposition results in formation of highly ordered crystalline material, also called pyrolytic BN. It is noteworthy that under some conditions an isotropic form of BN is obtained by vapor deposition.[119] This material may be an analogue of porous, glassy carbon obtained in some CVD processes or by pyrolysis of organic polymers.

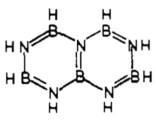
## *VI. Condensed-Phase Pyrolysis of Molecular Reagents*

A large number of molecular boron–nitrogen compounds have been prepared in the past 40 years;[120–125] therefore, it is at first surprising that there have been few published attempts to use molecular compounds to form h-BN by bulk, condensed-phase, thermal decomposition. This may be for good reason since there are potential drawbacks. For example, many molecular reagents contain significant amounts of carbon in organic substituent groups, and it is normally assumed that these groups must be removed during thermal processing. This usually requires a gaseous reducing atmosphere (e.g., $NH_3$ or $H_2$) to assist in B–C or N–C cleavage reactions. Otherwise, incorporation of carbon is expected to be prevalent, particularly when B–C bonds are present in the molecular reagent. If pure BN is required in an application, carbon contamination sources probably cannot be tolerated. However, it should be pointed out that controlled inclusion of carbon in BN may provide some useful mechanical properties.

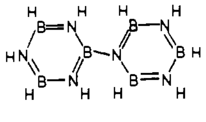
An additional practical hurdle involves reagent volatility. In CVD processing one would prefer to employ molecular species that have measurable volatility (1–100 Torr) in the temperature range −80 to +100 °C. However, for direct condensed-phase pyrolysis processing, it is preferable to have very low vapor pressures in the starting reagent or in its first >B–N< thermolysis product(s). This is a result of simple experimental design facts. For example, it is desirable to perform molecular pyrolyses in increasing temperature steps. In order to reduce substituent group contamination, e.g., carbon from organic residues, it is also useful to accomplish the pyrolyses under partial or full vacuum or under a flowing inert gas stream. Clearly, if the primary molecular reagents are volatile, they too will be removed from the reactor. Even if the pyrolyses are initially accomplished in a static atmosphere, volatile precursors will continually reflux out of the hot zone, thereby slowing or even modifying the decomposition chemistry. For these reasons and other molecule-specific shortcomings, an otherwise long list of potential molecular h-BN precursors is reduced to a handful of molecules. Of course, ingenious substituent group modifications could open up expansive new opportunities for molecular precursor processing to BN.

Compounds that have been surveyed as molecular precursors include several boron–nitrogen heterocycles, and much of the molecular chemistry of these compounds has been reviewed.[120–125] Pyrolyses of the parent borazene ($(HBNH)_3$ (**1**)), borazene derivatives, and reagents that produce borazene have attracted the most attention.

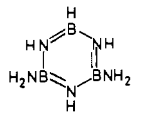
Stock and Pohland[126] first reported formation of borazene ($(HBNH)_3$) from the thermolysis (200 °C) of the addition complex $[H_2B(NH_2)_2^+][BH_4^-]$,[127] formulated in 1926 as $B_2H_6\cdot 2NH_3$. Subsequent pyrolysis at 500 °C led to an insoluble solid compound of empirical composition BNH that, upon pyrolysis at 900 °C, lost further hydrogen. Wiberg[128] then proposed that BNH was a polymer with an extended $(B{-}N)_n$ network and that its pyrolysis product was boron nitride. Laubengayer and co-workers[129] studied the gas-phase pyrolysis of $(HBNH)_3$ in greater detail, and they proposed the intermediate formation of a naphthalene analogue, $B_5N_5H_8$ (**2**), a biphenyl analogue, $B_6N_6H_{10}$ (**3**), and $(HB)(H_2NB)_2(NH)_3$ (**4**). Mamantov and Margrave[130] studied the decomposition of liquid borazene at ambient temperature, and they also detected formation of



$B_5N_5H_8$ 2

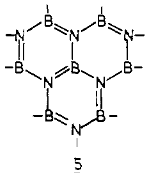


$B_6N_6H_{10}$ 3



$(HB)(H_2NB)_2(NH)_3$ 4

$B_5N_5H_8$ and $B_6N_6H_{10}$ by mass spectrometry. Additional high molecular weight polycyclic borazenes have not been isolated from gas-phase or liquid-phase borazene thermolyses, but a buildup process involving fused-ring condensation chemistry has been further justified by the isolation and molecular structure determination for **2** by Beck and Sneddon[131] and the preparation and molecular structure determination for a phenalene analogue $B_6N_7(SMe)_3(SiMe_3)_6$ (**5**) by Gasparis-Ebeling and Nöth[132] via a stepwise assembly reaction (idealized by structure **5**).



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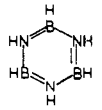
In experiments that may well have importance to interpretations of the CVD processing of borazene, Neiss and Porter[133,134] have reported on photoinduced (184.9 nm) condensation of gaseous borazene 1. By using mass spectrometry, they detected the formation of intermediates $B_5N_5H_8$ (**2**) and $B_6N_6H_{10}$ (**3**), and they observed the deposition of a polymer. It is of interest to determine if the photopolymer observed by Porter can be converted directly to h-BN or c-BN upon controlled pyrolysis, and experiments addressing this issue are in progress in our laboratory. In related work, Paffett and co-workers[135] have recently examined the vapor deposition of borazene on single-crystal metal substrates (Pt(001), Ru(001)), and a complete analysis of the borazene–metal surface interactions was accomplished.



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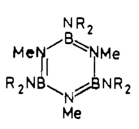
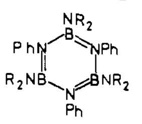
Building on Porter's photochemistry, Hirano and co-workers[136] have pyrolyzed $(HBNH)_3$ under constant pressure (100 mPa) between 250 and 700 °C in a sealed gold capsule. They obtained an amorphous form of BN that retains some B–H and N–H bonds as indicated by infrared spectra. These investigators also found that the introduction of AlN to the amorphous BN followed by pyrolysis at 1800 °C and 6.5 GPa gave c-BN.

Toeniskoetter and Hall[137] have thoroughly described the pyrolysis chemistry at 400 °C for a series of *B*-triamino-, *B*-tris(methylamino)-, and *B*-tris(dimethylamino) derivatives of *N*-trimethyl- and *N*-triphenylborazenes. Unfortunately, higher temperature pyrolyses were not examined; therefore, BN was not formed.



R= H or Me



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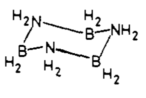

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Nonetheless, this paper contains interesting proposals regarding the mechanism of thermally activated borazene ring-opening processes that may be pertinent to the borazene polymer pyrolysis studies outlined in section VII.

Borazanes (parent = $H_6B_3N_3H_6$ (**6**)) should be useful molecular precursors for boron nitride formation; however, there are few appropriate molecules available for study.[120] Ammonia–borane(3), $H_3B{\cdot}NH_3$, is a well-known adduct described by Shore and Parry,[127] and its thermal chemistry has been partially explored by Geanangle[138] at 130–140 °C. A slightly soluble white solid was isolated from the low-temperature pyrolysis, and it was assigned a composition $H_2BNH_2$. Pyrolysis of this material between 500 and 600 °C gave a solid that was characterized only by its infrared spectrum that was comparable with that of h-BN.[139] Dahl and Schaeffer[140] reported a convenient preparation for the parent borazane compound $(H_2BNH_2)_3$ from the reaction of $NaBH_4$ and $(HBNH)_3{\cdot}HCl$ in diglyme. The thermolysis of this compound has not been fully explored, but heating a sample at 205 °C gave hydrogen and borazene as products. Presumably, subsequent pyrolysis chemistry would parallel that of $(HBNH)_3$.

Sneddon and co-workers[141] have discovered a wonderfully simple precursor system based upon straightforward Lewis acid–base chemistry. Commercially available $Me_2S{\cdot}B(H)Br_2$ was combined with gaseous $NH_3$, and the resulting unstable adduct, $H_3N{\cdot}B(H)Br_2$, when directly pyrolyzed at temperatures between 650 and 1500 °C, was converted to h-BN. This system is useful for forming powders as well as coatings on substrates. Substrates can simply be dipped into a solution containing $Me_2S{\cdot}B(H)Br_2$ and then pyrolyzed in an ammonia atmosphere.

Yogo and co-workers[142] have reported pyrolysis of a compound that is referred to as "triammonia decaborane" in $NH_3$. There is no precedent for the formation of a triammoniate of decaborane; however, it may well be $B_{10}H_{12}{\cdot}2NH_3$. Pyrolysis of the solid at 800 °C and then above 1180 °C gave h-BN. Further studies of the crystallization of the solid obtained at 800 °C was accomplished by heating at 1500 °C and 2.0-GPa pressure.

Polushin and Burdina[143] have reported on the pyrolysis of an adduct $Al(BH_4)_3{\cdot}4NH_3$ under several conditions. At 600 °C and <5.0 GPa, a mixture of h-BN and AlN was obtained, and at 900–1000 °C and 5–7 GPa, c-BN was formed. This is a particularly interesting system; however, anyone considering repeating this work should be aware of the fickle and potentially explosive decomposition chemistry of $Al(BH_4)_3$.

The limited attention given to molecular precursors suggests that there are numerous chemical nuggets residing in the old literature that may be useful in ceramics processing. This opinion is substantiated by the simple but novel discovery of Sneddon and co-workers.[141] Further systematic studies of systems that offer chemical simplicity, safety, and flexibility are warranted.

## *VII. Preceramic Polymer Routes*

Although improvements in conventional ceramic powder processing are welcome[144] and routes to finer powders are in demand, the fundamental shortcoming of most powders—their insoluble, infusible character—limits their utility in some advanced ceramics applications. Soluble and/or fusible preceramic polymers, despite their tendency to undergo shrinkage and chemical composition modification during pyrolysis, offer several unique benefits in the manufacture of complex, multifunctional materials, and a few representative examples are outlined here. For example, ceramic fibers embedded in a brittle ceramic or metal matrix are known to impart improved fracture toughness to the matrix.[36-38,145] Ceramic fibers cannot be prepared from a powder source, but they may be readily pulled or spun from a preceramic polymer.

Ceramics, due to their brittle character, must be shaped into articles by a variety of processing techniques that use a ceramic powder and a binder.[144] Many inorganic oxide and organic compounds have been employed as binders or auxiliaries to form green bodies,[146] but few impart favorable properties to the finished ceramic article if they remain after processing. Instead, additional steps must be introduced in the processing to bake the green body prior to final calcining. As a result, classical powder-forming procedures are multistepped, complex, costly, and not guaranteed to produce high-quality finished products. Polymeric precursors that convert to shaped articles without complex processing or that provide favorable composite properties with a powder would alleviate many processing problems and would be of great value.

Ceramic coatings recently have been prepared by CVD techniques, but in some applications the coatings obtained have poor performance characteristics. Polymeric precursors offer an alternate route to forming advanced ceramic coatings. Lastly, traditional powder processing does not provide a means to obtain articles with designed porosity. Polymeric precursors, together with sol–gel and aerogel processing techniques, provide a means to obtain such low-density, high-porosity articles.

The concept of forming non-oxide ceramics by polymer pyrolysis chemistry took its development cue from the successful processing of organic polymers into carbon fibers and bodies.[147] Early reports on pyrolyses of main-group polymers include those by Ainger and Herbert (PN),[148] Popper (BN, AlN, $Si_3N_4$, SiC),[149] Verbeek ($Si_3N_4$–SiC),[150] West[151] and Yajima[152] (SiC), Taniguchi (BN),[153] and Rice, Wynne, and Fox (SiC–$B_4C$).[154] The promise offered by these studies stimulated three forward-looking reviews on preceramic polymers by Rice[155,156] and Wynne and Rice.[157] These papers, together with the pressing demands for advanced materials, have spawned the current activity in inorganic polymer processing.

As might be expected when attempting to prepare high-quality ceramics, not just any polymer will serve as a useful precursor. Seyferth[158] has succinctly summarized the features that make a polymer useful as a preceramic. He suggests that in designing a polymer precursor it is particularly important that the monomer is readily available and inexpensive; the polymer chemistry is simple and proceeds with high yield; the polymer is liquid, fusible, or soluble in an organic solvent; the polymer is preferably stable in air at 25 °C; the pyrolysis chemistry proceeds smoothly in high yield with a minimum of violent gas evolution and a minimum of shrinkage; and the pyrolysis off gases are nonhazardous.

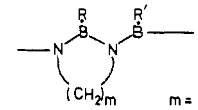
In addition to these practical considerations, one must pay close attention to certain chemical facts. For example, it is important to realize that many long-chain *linear* inorganic polymers self-destruct upon pyrolysis by evolution of small, volatile cyclic units. As a result, large amounts of the precursor building block are lost to the gas phase and ceramic yields are low. In order to overcome this tendency, reactivity centers or cross-links are built into the polymer that are thermally or photochemically activated. The degree of cross-linking must then be carefully varied with consideration of the application for the polymer, e.g., fibers, coatings, or foams.

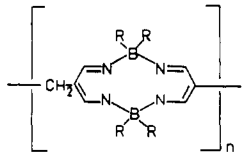
To prevent incorporation of deleterious impurity elements in the final ceramic, care must be exercised over the elemental and structural composition of the monomer and polymer. In turn, this requires an intimate knowledge of the thermodynamics and kinetics of inorganic reactions taking place in the formation of the monomer and polymer and occurring in the subsequent cross-linking and calcining process steps. We are deficient in our knowledge on how to accomplish the designed formulation of advanced ceramics from polymer precursors, and it is in this area that we probably know the least.

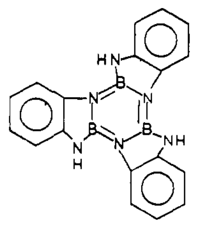
In the following paragraphs, the efforts of several research groups to design preceramic polymers suitable for conversion to boron nitride are summarized. The chemistry is presented not in any chronological order, but instead approximately in terms of the nature of the monomer(s) employed. Any reader new to this field should be aware that during the period 1940–1965, there was a concerted effort underway among inorganic chemists to prepare a number of inorganic polymers, including polymeric B–N compounds. The majority of that work has been thoroughly summarized in several reviews.[120-123,159] The intent of the early polymer studies was not to obtain ceramic products, and few descriptions of pyrolysis chemistry were given. Except where important to recent work, the early chemistry will not be discussed here.

Economy and Anderson[45] may be able to lay claim to the first polymer precursor route to h-BN in which the ceramic was clearly identified. They examined the reactions between trialkoxyboroxines and $NH_3$, and they isolated compounds of the type $(RO)_3B_{25}O_{36}(NH_3)_8$. The stoichiometries of the compounds deduced by elemental analyses were variable, and the structures of the polymers were not fully elucidated. However, when the polymer with R = *i*-PrO was pyrolyzed, first at 500 °C under $NH_3$ and then at 800 °C under $NH_3$, the residue obtained was identified as partially ordered, turbostratic BN. In somewhat related chemistry, Kato and co-workers[160] reported the formation of a spinnable condensation product from the reaction of boric acid and 1,2,3-propanetriol. This material was then heated at 1300–1400 °C for 2–4 h. Powder X-ray diffraction analysis of the resulting powder gave evidence of the formation of h-BN and $B_4C$, although the XRD patterns suggested limited crystallinity in the samples. In a more recent study, Kato[161] reported reactions between boric acid and diethanolamine as well as triethanolamine. These reactions produced a glassy polymer and a monomeric compound, respectively. Pyrolysis of the compounds under $N_2$ at 1400 °C was reported to give boron nitride and small amounts of $B_4C$. None of these studies provided data on ceramic yields, powder quality, or the utility of the intermediate polymers to form fibers or coatings.

In a completely different approach, early attempts were made to polymerize amine and aminoborane compounds.[162] Some success was apparently achieved, but the characterization of the polymers was limited. No attempt to convert these materials to ceramics was reported because this was not a goal at the time. More recently, Neilson and co-workers[163] have reported initial efforts to form linear polymers based on 1,3,2-diazaboracycloalkane ring systems. The conversion of these polymers to ceramic products has not been reported. Maya[164] has recently reported on reactions of $BEt_3$ and $B(NMe_2)_3$ with polyfunctional amines and on the subsequent pyrolysis of resulting polymers. He found that polymers with high aromatic carbon content, e.g., pyrazabole and *o*-phenylenediaminoborazenes, provided useful precursors for formation of B–C–N films.

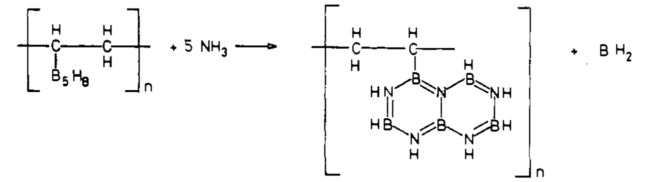






Boron hydrides offer an attractive monomer feedstock for the production of B–N polymers, and some efforts have been reported that utilize $B_{10}H_{14}$ and $B_5H_9$. Johnson[165] and Rees and Seyferth[166] have extended some well-known acid–base chemistry of the $B_{10}H_{14}$ cage,[167] and they have isolated several soluble polymers containing $B_{10}H_{12}$ units cross-linked by amine or phosphine units. Pyrolysis of $[B_{10}H_{12}N(H_2)CH_2CH_2N(H_2)]_n$ under $NH_3$ at 1000 °C gave white boron nitride in 62% ceramic yield.[166] Prior to pyrolysis, the polymer was also used as a binder with powdered BN to form a ceramic bar. Fibers were drawn from a solution syrup of the polymer, and they were pyrolyzed under $NH_3$. The parent polymer and analogues carrying methyl groups on the nitrogen atoms, when pyrolyzed under Ar first at 1000 °C and then at 1500 °C, produced powders that contained BN and $B_4C$. These polymers also were used to form monoliths, fibers, and binders. Related polymers with phosphine cross-linkers produced ceramic solids containing phosphorus.[166]

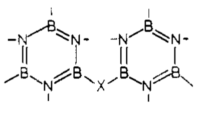
Mirabelli and Sneddon[168] have found that 2-vinylpentaborane(8) undergoes polymerization with the resulting formation of soluble poly(2-vinylpentaborane). Subsequently, they observed that pyrolysis of this material in $NH_3$ under a specific thermal schedule produced amorphous BN containing a small amount of carbon.[169] The amorphous BN was converted to h-BN in high overall ceramic yield by further heating of the residue at 1450 °C. A particularly interesting feature of this chemistry is that, unlike most ceramic precursors, in theory there should be a weight *gain* upon conversion of the poly(2-vinylpentaborane) precursor to the BN ceramic product, and in fact a minimal weight gain is detected. Attempts to characterize the polymeric thermal intermediates led to a suggestion that pendant $B_5H_8$ units in the poly(2-vinylpentaborane) are converted to pendant borazanaphthalene units as schematically depicted below. This concept is reminiscent of the photoinduced borazene polymerization chemistry,[133,134] as well as the incompletely characterized thermal chemistry of ammonia–borane[138] and borazane which may produce fused-ring products.



In fact, the boron precursor family that has attracted the greatest attention in the formulation of preceramic polymers for conversion to boron nitride is borazene and its derivatives. Although Lappert[159] described the potential stability and structural relationships between polyborazenes and boron nitride, it was also pointed out[120–123,159] that polyborazenes were insoluble, infusible, and essentially impossible to process probably as a result of significant cross-linking chemistry even at relatively low temperatures. This suggested that polyborazenes might be useless as advanced preceramics. Nonetheless, enough promise was shown in these studies that several groups have revisited polyborazenes as ceramic precursors. A summary of some of the older polyborazene work is provided now as an introduction to the more current work in progress.

Wagner and Bradford[170] attempted to prepare the borazene analogues of naphthalene and biphenyl mentioned in section V by direct borazene dehydrogenation reactions. For example, pyrolysis of a mixture of 2,3,4,5,6-pentamethylborazene and 1,3,4,5,6-pentamethylborazene might be expected to produce decamethyl-*N*,*B*′-diborazinyl, but no evidence of this product was found. This compound was instead obtained by LiCl elimination from *N*-lithiopentamethylborazene and *B*-chloropentamethylborazene.[170] This chemistry was extended to include the reaction of *N*-dilithiotetramethylborazene and *B*-dichlorotetramethylborazene that gave a polyborazinyl chain estimated to contain 10 borazene rings. The polymer melted in the range 155–168 °C. Although some polymer characteristics are described in a parent, there appears to have been no further work to exploit them. Indeed, removing the large number of *B*-methyl and *N*-methyl groups would be expected to be difficult even under reducing pyrolysis conditions. In a different approach to achieve direct *N*–*B*′-borazene ring condensations, Gerrard and co-workers[171] heated 2,4,6-*B*-triaminoborazenes, $(R_2NBNH)_3$, in the range 200–400 °C under reduced pressure. Polymeric, insoluble products were obtained, but they were only partially characterized.

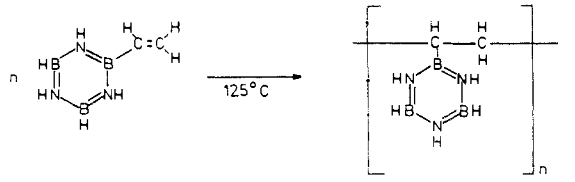
The cross-linking of borazene rings with an NR group was reported by Lappert[172] in 1959, and since then a number of cross-linking studies have appeared. Cross-linker atoms or groups, X, that have been employed include –O–,[170,173–178] $-OSi(R)_2O-$,[179] $-OP(O)(OR)O-$,[180,181] $-C(O)N(H)(CH_2)_6N(H)C(O)-$,[182] –C-



$(CH_3)_2$–,[183] –S–,[184] –N(R)P(O)(R)N(R)–,[185] and –N(R)–.[170,186–189] Few of these polymers have been characterized in detail, and most appear to be completely intractable. The thermal chemistry was examined for the most part at very modest temperatures, and no attempts to form ceramic products were described in these studies. It is worth noting that the –O–, –N($CH_3$)–, and –N(H)– cross-linked tetramethylborazene polymers described by Meller have some solubility, and we will return to this chemistry again.

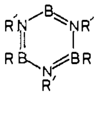
During the course of Meller's studies, the first direct attempts to use a polyborazinyl reagent as a ceramic precursor was reported by Taniguchi[190] in a Japanese patent filing. It was claimed that when 2,4,6-*B*-triamino-1,3,5-*N*-triphenylborazene (($H_2NBNPh)_3$) was heated at 250 °C under $N_2$ for 4 h, a polymer was obtained with a softening temperature of 150–200 °C. It was further claimed that the polymer formed a melt at 220 °C that could be formed into fibers, and at 300 °C, it could be used to deposit a film. No *specific* mention was made in the patent abstract that the polymer could be converted to boron nitride. In a later patent report, Taniguchi[191] claimed that various substituted borazenes formed polymers, and these could be used to form BN, or they could be used as a binder with BN powder. Attempts to reproduce this work in at least one group have not been successful.[192,193]

Recently, there have been some fresh looks at routes to polyborazene precursors. Lynch and Sneddon[194] have reported the formation of *B*-vinylborazenes from $Rh(H)(CO)(PPh_3)_3$-catalyzed addition of borazene and acetylene at 25 °C. Gentle thermolysis of this material at 120 °C produced an insoluble, rubbery polymer schematically represented below. However, reaction of *B*-alkenylborazene with excess (50 mol %) borazene at 125 °C produced an initially viscous polymer that is soluble in $C_6H_6$, $Et_2O$, and THF. Heating this polymer for extended periods resulted in formation of an insoluble polymer. Pyrolyses of these polymers were carefully studied under Ar and $N_2$. It was found that turbostratic BN with significant inclusions of carbon was produced. The carbon content in the first polymer was dramatically reduced when it was heated in $NH_3$. The lowest levels of contamination were obtained when the second polymer was heated under $NH_3$ at 1000 °C. The ceramic residue from the second polymer was heated at 1450 °C under Ar, and white h-BN was obtained as evidenced by its density and XRD pattern. The polymer chemistry was found to be general for the formation of other poly(alkenylborazenes); however, their conversion to ceramic products has not yet been described.



In a recently issued patent, Blum and Laine[195] claimed generalized procedures for forming group III–V preceramic polymers. The processes involve metal-catalyzed dehydro–coupling–condensation reactions between monomers containing, for example, one or more B–H bonds and one or more N–H bonds. Pyrolyses of several polymers are mentioned in the patent; however, it is not clear that crystalline boron nitride was obtained from these systems. Further work will be required to settle this point.

In the past few years, Paciorek and co-workers[192,193,196–200] and Rice and co-workers[201,202] have examined syntheses and processing of a number of borazene monomers and polymers as boron nitride precursors. In 1984, Paciorek[192] briefly reported on the pyrolysis of a series of borazene monomers without indicating if the monomers produced boron nitride. In 1985, a brief summary of the Ultrasystems project was published in an Office of Naval Research government report.[193] It was stated in the report that *B*-trichloro-*N*-triphenylborazene, *B*-triamino-*N*-trimethylborazene, *B*-triamino-*N*-triphenylborazine, *B*-trianilinoborazene, *B*-trichloro-*N*-tris(trimethylsilyl)borazene, *B*-triamino-*N*-tris(trimethylsilyl)borazene, and *B*-tris[bis(trimethylsilyl)amino]borazene were prepared, and their pyrolysis chemistry was studied with the objective of discovering preceramic polymers suitable for formation of boron nitride fibers and coatings. It was concluded that halo-substituted borazenes produced glassy products, and the *B*-amino-*N*-alkyl-substituted borazene was unsatisfactory due to its volatility and tendency to evolve ammonia. The *N*-phenyl-substituted borazenes (homo- and copolymer) gave high melting points, and pyrolyses (1000 °C) left black products that contained carbon. *B*-Tris[bis(trimethylsilyl)amino]borazene was found to be stable up to 400 °C. Heating *B*-triamino-*N*-tris(trimethylsilyl)borazene at 65–227 °C gave a polymer from which pure boron nitride fibers were drawn and then cured in an $NH_3$ atmosphere at 75–970 °C. It was also suggested in this report that pyrolysis of the monomers on the way to formation of polymeric products proceeded stepwise by borazene ring opening and closing processes of the type discussed by Toeniskoetter and Hall.[137]



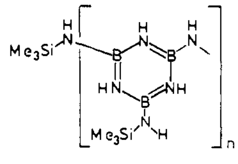
| R = | $NH_2$ | $NH_2$ | NH(Ph) |
|---|---|---|---|
| R = | Ph | Me | H |

At about the same time, working together with Ultrasystems, Rice and co-workers[201] described the conceptual relationship between graphite and h-BN and their plan to form boron nitride from preceramic polymers in a fashion similar to that described for graphite and SiC. They also described initial pyrolysis studies of several substituted borazenes that produced boron-rich, carbon-contaminated products.

In 1986, a patent report[196] appeared from the Ultrasystems group that outlined the formation of polymers from *B*-triamino-*N*-tris(trialkylsilyl)borazenes mentioned above.[193] In addition, a paper appeared[197] that provided some details on the results of borazene pyrolysis studies mentioned in the ONR report.[193] They also outlined a pictorial mechanism for the polymer to ceramic condensation process.

In 1988, Paciorek and co-workers[198,199] again described the formation of a fusible, soluble preceramic polymer from *B*-triamino-*N*-tris(trimethylsilyl)borazene heated at 200 °C, and additional details on preparation and processing were provided to supplement the earlier report.[193] The polymer was melt spun into 11–20-μm monofilament, and the fibers were slowly calcined over 98 h under ammonia at 50–1000 °C. Although the synthesis of the borazene monomer at present involves a troublesome multistep process, the processing results appear to be very promising. Paciorek indicates that further studies of these fibers are in progress.

In a patent report[200] and a paper,[198] Paciorek and co-workers also described the formation of the polymer shown schematically below, from the reaction of *B*-trichloroborazene and hexamethyldisilazane. This polymer was reported to be infusible, but soluble in pentane and hexane. The polymer solution was used to coat alumina fibers, and then the polymer was converted to a boron nitride coating. This provides a ready means for protecting the ceramic fibers as well as producing ceramic–ceramic composites. It will also be seen shortly that this work closely parallels investigations in our own laboratory. Together, these investigations are providing a set of polyborazinyl preceramic polymers that may be suitable for commercial applications.



Pursuing other chemical systems, Paciorek and Wynne[198,203,204] have recently begun to explore routes to BN polymeric precursors that utilize noncyclic silylaminoborane monomers. The foundations have been set with the reports on monomer chemistry, and it can be anticipated that polymer chemistry will be forthcoming.

In 1984, stimulated by a Materials Research Society Symposium "Better Ceramics through Chemistry—I",[205] we embarked on studies aimed at preparing non-oxide preceramic polymers by methods related to sol–gel techniques already in use for processing silica and other oxides. In a manner made popular by organic polymer chemists, we reasoned that tractable BN polymers might be obtained in an organic solvent by two-dimensional and three-dimensional cross-linking of boron–nitrogen ring compounds. Such polymers with appropriate compositions, easily removed exo substituents, modest ring bond energies, and favorable structural flexibility about cross-linking arms should take part in thermally activated monomer ring opening and condensation reactions. Under favorable steric and electronic conditions, these processes should lead to reassembled solid-state structures having the extended array of atoms found in the graphitic h-BN structure.

We initially chose to explore sol–gel-like condensations to prepare polyborazinyl compounds. This selection was made despite indications in the literature that polyborazenes formed intractable polymers in thermally driven elimination–condensation reactions. Specifically, we chose to revisit polyborazinylamine chemistry initiated by Lappert[172] and subsequently elaborated in more detail by Meller.[186–189]

In order to model the condensation polymerization reactions of interest, we first examined model amination reactions of the type shown in eq 1.[206]

$$R_2BCl + R'_2NSiMe_3 \rightarrow R_2BNR'_2 + Me_3SiCl \quad (1)$$

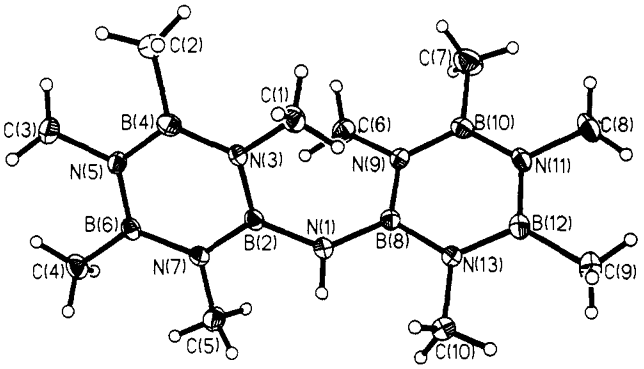


**Figure 4.** Molecular structure for bisborazinylamine **7**, $[(MeN)_3(MeB)_2B]_2NH$.

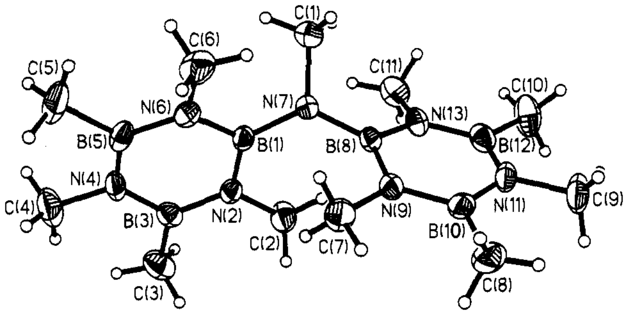
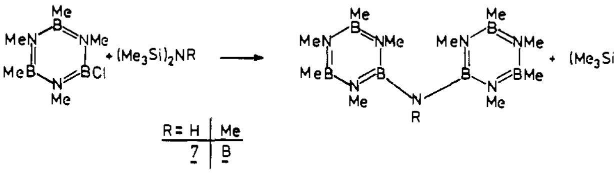


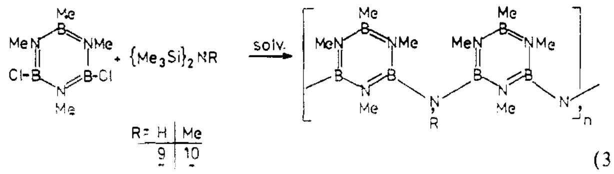
**Figure 5.** Molecular structure for bisborazinylmethylamine **8**, $[(MeN)_3(MeB)_2B]_2NMe$.

The driving force in these reactions is the formation of stable, volatile $Me_3SiCl$. Indeed, reactions of 2-chloro-1,3,4,5,6-pentamethylborazene with hexamethyldisilazane and heptamethyldisilazane lead to the corresponding bisborazinylamines, **7** and **8**, in high yields as described in eq 2.[207–209] These crystalline compounds have been fully characterized by spectroscopic methods. Single-crystal X-ray diffraction analyses have been completed for both derivatives,[209] and views are shown in Figures 4 and 5. The structures reveal that the cross-linking nitrogen atoms –N(H)– and –N($CH_3$)– are planar, and the borazene rings are twisted slightly out of the $B_2NH$ and $B_2NC$ planes. The average exo B–N and endo B–N bond distances in **7** are 1.444 (7) and 1.440 (5) Å, respectively. The average distances in **8** are 1.461 (5) and 1.430 (5) Å, respectively. The exo B–N distances are intermediate between the exo B–N distances in 2,4,6-tris(dimethylamino)borazene, 1.429 Å,[210] and 2-aminoborazene, 1.498 (8) Å.[211] The endo B–N distances fall in the expected range, 1.42–1.45 Å, derived from numerous borazene ring compounds. These distances suggest that the degree of π bonding is comparable between exo and endo B–N bonds. The thermal chemistry of these molecular reagents was not explored.



(2)

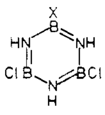
A borazene monomer with two sites available for cross-linking reactions should form a linear ("two point") polymer that might prove useful for forming a coating precursor. One such monomer is 2,4-dichloro-1,3,5,6-tetramethylborazene. Although the methyl groups will clearly limit cross-linking as desired, they also introduce the possibility of retaining carbon in the ceramic product. We examined the cross-linking reactions of this monomer with both hexamethyldisilazane and heptamethyldisilazane in chlorobenzene and $CH_2Cl_2$ as shown in eq 3.[209] Both reactions produce moisture-sensitive B-cross-linked oligomeric mixtures that are soluble in the reaction medium. If the solvent and volatile byproducts are removed, white solids **9** and **10** are obtained, and elemental analyses agree relatively well with the expected compositions. Solutions of **10** are useful for depositing the oligomer on substrates, although subsequent pyrolysis under nitrogen leaves a coating of carbon-contaminated h-BN on the substrate.



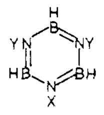
(3)

The pyrolysis chemistry of solid **10**, after removal of the solvent, has also been studied under various conditions.[209] As expected, pyrolysis performed under Ar or $N_2$ atmospheres results in the formation of black residues that contain significant amounts of carbon. Pyrolyses under $NH_3$ at 1200 °C result in a light gray residue (~25% ceramic yield) that contains h-BN and a variable amount of carbon. Although these "two-point" polymers are tractable prior to solvent removal and relatively easy to work with, the carbon contamination problem and low ceramic yields under some conditions led us to explore alternative coating systems. Further studies of these materials that may take advantage of the carbon inclusions are planned.

When considering other monomers as two-point polymer B-cross-linked or N-cross-linked precursors, it is important to evaluate the thermodynamic requirements for removing blocking groups from the other atoms. It is also necessary to consider the nature of the pyrolysis contaminants if the blocking groups remain in the polymer. Promising monomers are shown here as **11** and **12**. Examination of the borazene literature[120-125] reveals that there are few known examples of **11** or **12**. Further, not all blocking groups, X, that might be employed can be easily removed during polymer processing. Nonetheless, there are several monomers that warrant attention.

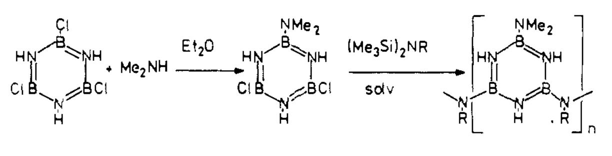


11

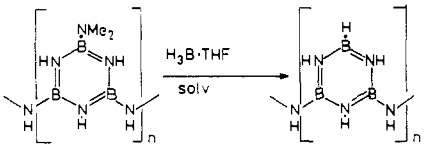


12

Specifically, we have examined the disilazane B-cross-linking chemistry of 2-(dimethylamino)-4,6-dichloroborazene (**11**; X = $NMe_2$) with hexamethyldisilazane in chlorobenzene, in hexane, or without solvent as shown in eq 4.[212] This monomer is attractive because it is known that the $NMe_2$ group can be replaced with hydrogen by reaction of the monomer with $H_3B{\cdot}THF$.[213] The composition and solubility of the polymeric product are dependent upon solvent and reaction temperature, and the polymers are not as soluble as expected. In chlorobenzene, a gel is formed that, upon removal of the solvent, leaves an insoluble glassy solid. Gels are not formed in hexane, and an insoluble solid is directly deposited. A gel is obtained when no solvent is used. The results of the pyrolyses are dependent upon several processing conditions. Briefly, we find that pyrolysis of the insoluble solid polymers produces good yields of h-BN when $NH_3$ is used as the pyrolysis atmosphere. When the gels or solids are exposed to the ambient atmosphere prior to pyrolysis and/or pyrolyzed under nitrogen, poor yields of carbon-contaminated boron nitride are obtained. Pyrolysis of the gel formed without solvent in an $NH_3$ atmosphere gives good yields of h-BN.



| R/solv. | H | Me |
|---|---|---|
| $C_6H_5Cl$ | 1 | 3 |
| hexane | 2 | 4 |
| neat | | 5 |



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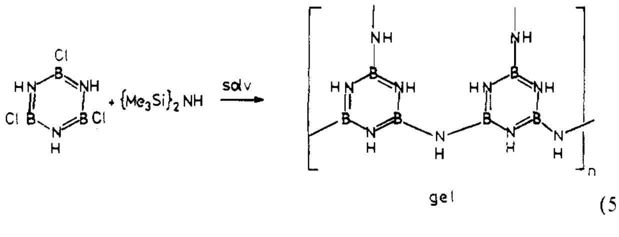
(4)

Since the monomer, $(Me_2NB)(BCl)_2(NH)_3$, can be converted to the carbon-free borazene, $(HB)(BCl)_2(NH)_3$, by reaction with $H_3B{\cdot}THF$, we anticipated that the polymer formed between $(Me_2NB)(BCl)_2(NH)_3$ and $(Me_3Si)_2NH$ might be converted to a carbon-free polymer if the $NMe_2$ blocking groups could be removed. In fact, this was accomplished by combination of the polymer with $H_3B{\cdot}THF$. The resulting polymer was pyrolyzed in $NH_3$ at 1200 °C, and a good yield of pure, crystalline h-BN was obtained. This chemistry illustrates that it is possible to employ a functionally blocked borazene monomer to construct a two-point cross-linked polymer. Further, it shows that, in the case of X = $NMe_2$, the blocking group can be chemically removed from the polymer at low temperature, and it verifies that pure h-BN is obtained from such a process. These positive results, however, do not offset the problem that these two-point polymers are not readily soluble or fusible. As a result, they have little practical utility for coating or fiber applications. However, if the polymer solubility can be increased, the scheme would have utility. Several variations of the carbon-free polymer and several other monomeric examples of **11** are under examination.

The synthesis of a three-point, or fully B-cross-linked, polymer from trichloroborazene has also been examined,[207,208,214] and the chemistry is outlined in eq 5. The



(5)

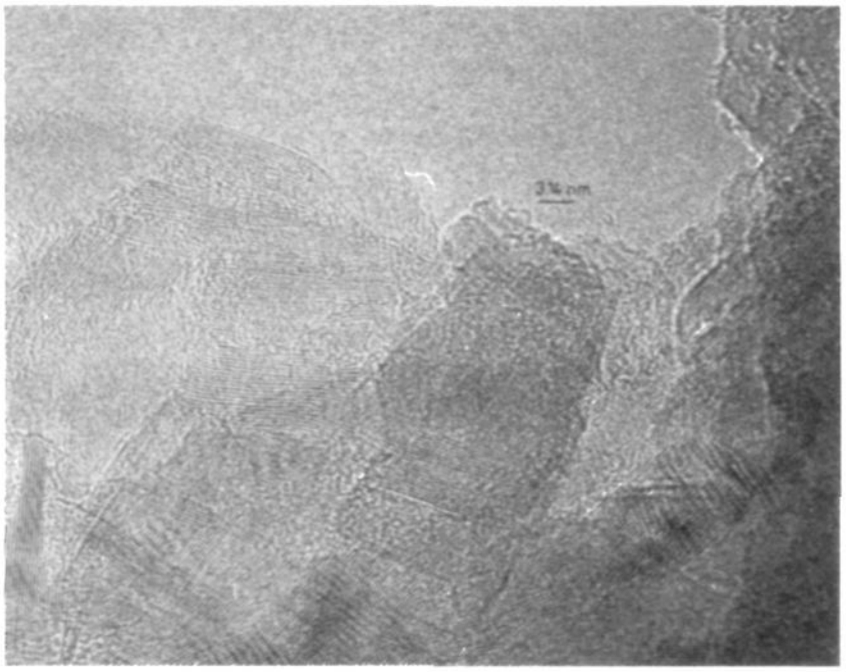


**Figure 6**. Transmission electron micrograph for h-BN powder obtained from pyrolysis of **13**.

reaction can be performed in a wide range of solvents. Gels (**13**) are obtained in each case. Prior to gelation, soluble oligomeric fragments can be deposited onto substrates by slow evaporation of the solvent. Pyrolysis under $N_2$ or $NH_3$ leaves thin films of h-BN on the substrates.

The early stages of the pyrolysis chemistry of the nitrogen- and hydrogen-rich polymer **13** formed either in diethyl ether (subsequently cast as a film on an Al substrate) or in THF (evaporated to dryness, redissolved in $NH_3$, and cast as a film on an Al substrate) have been carefully studied by thermal decomposition mass spectrometry (TDMS), XPS, and TGA.[215] It was observed that gas evolution accompanying thermal decomposition of the polymer in the TDMS high-vacuum chamber begins at ~100 °C, and it is essentially complete at 400 °C. The major thermal events occur abruptly between 200 and 300 °C, and $NH_3$ is identified as the primary product along with smaller amounts of $N_2$ and HCl. Since continued pyrolysis of the films produced h-BN between 1000 and 1200 °C, it can be concluded that the low-temperature gas evolution processes are not rate limiting in the formation of h-BN.

When bulk samples of the three-point gels, **13**, are evaporated to dryness and the resulting glassy solids are pyrolyzed uner nitrogen at 1200 °C, relatively pure h-BN powder is obtained with good ceramic yields (55–60%). Small amounts of silicon may be retained from pyrolysis of residual methylsilyl end-capping groups. The silicon may be completely removed by pyrolysis of the gel under $NH_3$ at 1200 °C. Alternatively, the ceramic powder obtained from pyrolysis under nitrogen may be briefly heated under air and washed under ambient conditions with aqueous HF solution. The XRD analysis of these powders shows the expected sharp lines, and TEM analysis reveals formation of highly crystalline grains. A typical micrograph is shown in Figure 6.

The results from these initial studies indicated that polyborazinylamines with low carbon content provide adequate precursors for the formation of h-BN powders. At first glance, these oligomers did not appear to be particularly useful for production of other forms of h-BN. However, during the course of our studies with **13**, two important and related observations were made.

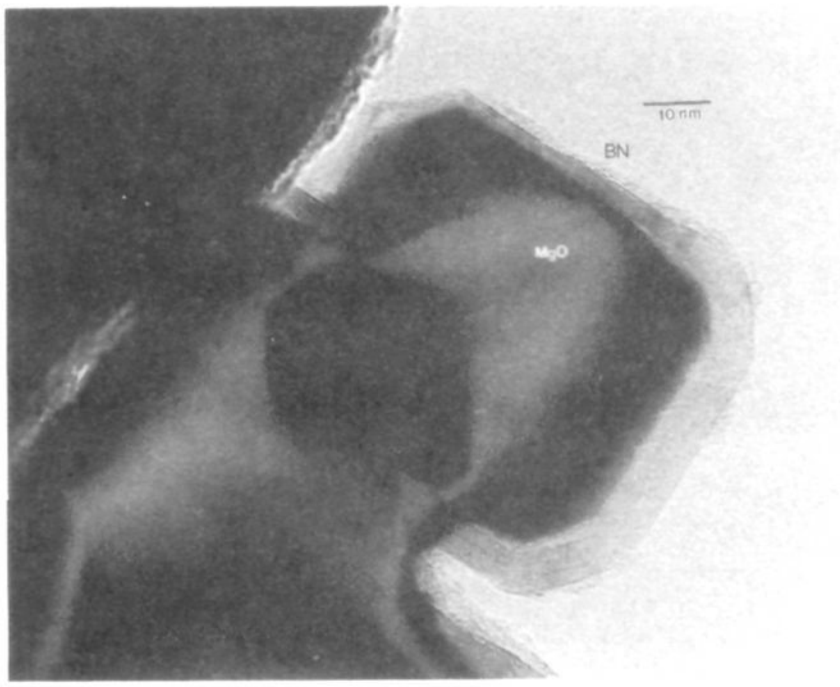


**Figure 7**. Transmission electron micrograph for h-BN deposited on single crystals of MgO.

When samples of **13** are exposed to liquid $NH_3$, the oligomer dissolves completely.[216,217] Subsequent evaporation of the $NH_3$ leaves a foamy white solid. TGA of this material under Ar shows a sharp weight loss (42%) between 25 and 350 °C and no further loss out to 1100 °C. This solid in contact with surface-activated substrates (e.g., surface hydroxyl groups) appears to "melt" or "flux" with the substrates at 1000–1200 °C, and upon cooling, the coatings crystallize as h-BN. High-quality, adherent coatings on MgO, $Al_2O_3$, and $TiO_2$ have now been studied in detail, and Figure 7 shows a typical transmission electron micrograph for a film deposited on MgO single crystals. This polymer, despite the high processing temperature, offers a unique reagent for forming BN coatings and composites. It also may be used in binder applications with ceramic powders and fibers. We are presently examining approaches to lower the melting temperature in order to facilitate fiber pulling from the melt.

The ammonia solutions of **13** have also been concentrated to the point that a heavy syrup is obtained. By using a simple fiber-pulling jig, we have succeeded in drawing green fibers from the syrup. Subsequent pyrolysis at 1200 °C in ammonia results in transparent BN fibers that are amorphous to X-rays. Continued pyrolysis of these fibers at 1500 °C under argon results in crystalline fibers.[218] We also have observed that concentrated ammonia solutions of **13** offer a useful approach to forming dense articles, depositing preceramic coatings by dipping and producing a composite matrix with ceramic fibers.[215,218,219]

One of our original objectives was to develop a method for producing a "low-density" or foam state for boron nitride with potential applications in composites. That goal has been achieved by using aerogel techniques.[220] For example, the gel may be initially formed in small bottles that allow transfer of the air-sensitive gel to a critical point dryer. Subsequent treatment (solvent exchange) with $CO_2$(l) and then $CO_2$(l) at its critical point leaves a polymer precursor pellet typically 1.5 cm × 2.2 cm in size. These pellets may be heated to 1200 °C with attendant shrinkage, and the resulting boron nitride article typically has 200–400 $m^2/g$ surface area.[221] Further heating at 1650 °C results in an article with a surface area of ~100 $m^2/g$. We have also re-

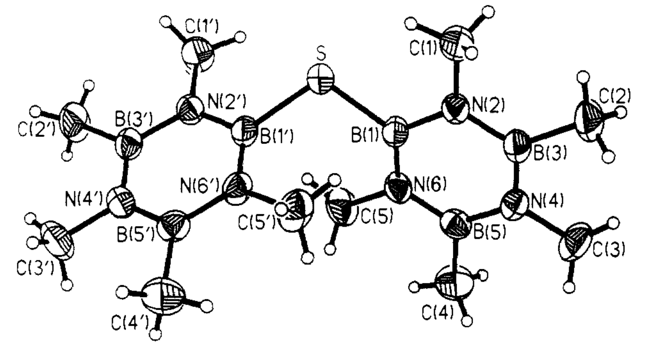
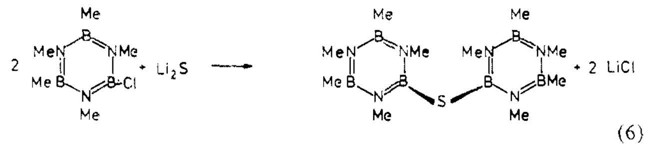


**Figure** 8. Molecular structure for bisborazinyl sulfide $[(MeN)_3(MeB)_2B]_2S$.

cently found that whiskers and fibers may be included in the original gel, and the resulting aerogel dried form has increased strength. Studies of these low-density materials are in progress.

Additional cross-linking chemistry is underway in our group, and a few specific details of work in progress are provided here. The exo and endo B–N bond distances in the model bisborazinylamine compounds, 7 and 8, suggested that these bonds are approximately equal in strength. The "carbon-free" gel, 13, is expected to have a related structure, but cross-linking involves all three boron atoms. It has an initial composition excess in nitrogen (N:B = 1.5), and the pyrolysis chemistry must remove the excess nitrogen. Indeed, this is seen as a benefit since this acts chemically as an "internal reductant". With reference to the mechanistic pictures of the thermal decomposition chemistry proposed by Toeniskoetter[137] and Paciorek,[197] it is interesting to speculate over which N group is evolved: N–H from the borazene ring or N–H from the bridging group. Nitrogen isotope labeling of the gel and thermal decomposition mass spectrometry studies clearly show statistical scrambling of $^{15}N$ and $^{14}N$ in the evolved $NH_3$ and $N_2$. This result argues in favor of ring-opening processes in the structural transition from polyborazinylamine to amorphous BN. Consistent with the labeling studies, we have also found that, when the gel cross-linking group is $NCH_3$, pyrolysis of a bulk sample produces $NH_3$, $CH_3NH_2$, $NH_4Cl$, and $CH_3NH_3Cl$ in the off gases.

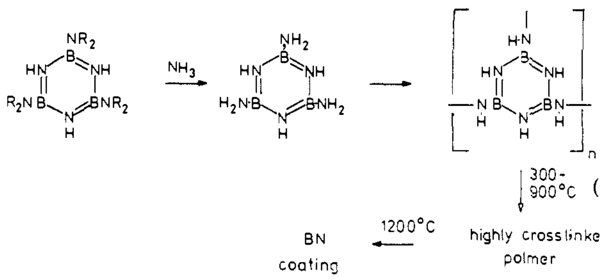
If weaker cross-linking groups are used to form the gel, it might be expected that the pyrolysis chemistry would be affected. We have examined the following groups: O, S, N(H)–N(H), PH, and $PSiMe_3$. A brief description of the chemistry obtained with a sulfur bridging group is provided. A model compound was formed from reaction of $Li_2S$ and 2-chloro-1,3,4,5,6-pentamethylborazene as shown in eq 6. The crystalline model compound was isolated and characterized by spectroscopic techniques, and the molecular structure was determined by X-ray diffraction methods. A view of the compound is shown in Figure 8. The two borazene rings are twisted with respect to each other, making an angle of 69.7°. The B–S bond distance is 1.851 (2) Å, and the average B–N distance is 1.433 Å.



(6)

A polyborazinyl sulfide gel related to that reported by Toeniskoetter[184] was obtained by combination of $Li_2S$ and 2,4,6-trichloroborazene in THF. Removal of the solvent left a solid polymer which was extracted with fresh THF to remove as much of the LiCl as possible. Subsequent pyrolysis at temperatures as low as 700 °C produced h-BN. The low crystallization temperature is believed to result from the presence of the LiCl. Additional pyrolysis and processing studies of this and other weakly cross-linked borazenes that may provide useful, tractable precursors are in progress.

One final reaction that has attracted our attention is described. Aminoborazenes[137,181] are known to undergo deamination reactions that produce bisborazinylamines or higher oligomers as shown in eq 7.



(7)

This reaction is so facile that aminolysis of $[(Et_2N)BNH]_3$,[171] $[(Me_2N)BNH]_3$,[222,223] and $[(BuS)BNH]_3$[224] are reported to give an insoluble polymeric solid formulated as $[(H_2N)BNH]_3$. We have observed that the aminolysis of $[(Me_2N)BNH]_3$ in toluene produces an insoluble white solid, and pyrolysis of the solid at 900 °C in vacuo followed by pyrolysis at 1200 °C in $NH_3$ or $N_2$ results in formation of excellent-quality h-BN in good yield (~50%).[225] Modifications of the pyrolysis scheme in fact improve the yield, and studies of this system continue.

## *VIII. Summary*

It can be seen by the diverse and unique chemistry and properties outlined here that boron nitride is a fascinating ceramic with a potentially bright future in advanced materials design. However, before most of its potential can be realized, a number of unsolved chemical synthesis and processing problems need to be addressed head on and solved. As has been the case with $Si_3N_4$ and SiC, molecular and polymer-based syntheses, in particular, offer considerable promise for achieving unmet chemical synthesis needs for fiber, coating, and porous-body boron nitride forms. Work on unique ceramic precursors will certainly be rewarding and beneficial. In addition, there is need for more detailed physical property studies on BN samples that are well characterized. The opportunities involving incorporation of BN in composites are immense, and chemists should turn attention to careful molecular level phase interaction and surface modification studies that will address mechanisms for critical solid-state materials behavior, e.g., cracking. Lastly, we point out that there are great opportunities for fruitful collaborations between chemists, physicists, materials scientists, and engineers on problems that are fundamentally challenging and of intrinsic scientific interest as well as crucially important to the commercial advanced materials industry.

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**Registry No.** Boron nitride, 10043-11-5.

## IX. References

(1) Kingery, W. D.; Bowen, H. K.; Ullman, D. R. *Introduction to Ceramics*, 2nd ed.; Wiley: New York, 1976.
(2) Archer, N. J. *Spec. Publ. Chem. Soc. (London)* **1977**, *No. 30*, 167; *Chem. Abstr.* **1978**, *88*, 65011.
(3) (a) Meller, A. *Gmelin Handbuch der Anorganische Chemie, Boron Compounds*; Springer-Verlag: Berlin, 1983; 2nd Supplement, Vol. 1, p 20; (b) Meller, A. *Gmelin Handbuch der Anorganische Chemie, Boron Compounds*; Springer-Verlag: Berlin, 1988; 3rd Supplement, Vol. 3, p 1 and references therein.
(4) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1984.
(5) Akashi, T.; Pak, H.-R.; Sawaoka, A. B. *J. Mater. Sci.* **1986**, *21*, 4060.
(6) Sokolowski, M. *J. Cryst. Growth* **1979**, *46*, 136.
(7) Szmidt, J.; Jakubowski, A.; Michaeski, A.; Rusek, A. *Thin Solid Films* **1983**, *110*, 7.
(8) Kessler, G.; Bauer, H.-D.; Pampe, W.; Scheibe, H.-J. *Thin Solid Films* **1987**, *147*, L45.
(9) Rather, B.; Zscheile, H. D.; Weissmantel, C. *Thin Solid Films* **1986**, *142*, 83.
(10) Thomas, J.; Weston, N. E.; O'Connor, T. E. *J. Am. Chem. Soc.* **1962**, *84*, 4619.
(11) Pease, R. S. *Acta Crystallogr.* **1952**, *5*, 356.
(12) Powell, C. F.; Oxley, J. H.; Blocher, J. M., Jr. *Vapor Deposition*; Wiley: New York, 1966.
(13) Kalyoncu, R. S. *Ceram. Eng. Sci. Proc.* **1985**, *6*, 1356.
(14) Hove, J. E.; Riley, W. C. *Modern Ceramics: Some Principles and Concepts*; Wiley: New York, 1965. Kendall, E. G. *Ceramics for Advanced Technologies*; Hove, J. E., Riley, W. C., Eds.; Wiley: New York, 1965.
(15) Hoffman, D. M.; Doll, G. L.; Eklund, P. C. *Phys. Rev. B* **1984**, *30*, 6051.
(16) Kotlensky, W. V.; Martens, H. E. *Nature* **1962**, *196*, 1090.
(17) Moore, A. W. *Nature* **1969**, *221*, 1133.
(18) "Pyrolytic Boron Nitride Materials Data Sheet", GTE Products Corp., Exeter, NH. A summary of some properties of hot-pressed BN may be found in ref 44.
(19) Lozier, W. W.; Manofsky, M. B. Properties and Performance of Pyrolytic Graphite. In *Mechanical Properties of Engineering Ceramics*; Kriegel, W. W., Palmour, H., III, Eds.; Interscience: New York, 1961.
(20) Butenko, V. A.; Lopatin, V. V.; Cherneko, V. P. *Inorg. Mater. (Engl. Transl.)* **1984**, *20*, 1428.
(21) Miller, F. A.; Wilkins, C. H. *Anal. Chem.* **1952**, *24*, 1253.
(22) Brame, E. G., Jr.; Margrave, J. L.; Meloche, V. W. *J. Inorg. Nucl. Chem.* **1957**, *5*, 48.
(23) Li, P.-C.; Lepie, M. P. *J. Am. Ceram. Soc.* **1965**, *48*, 277.
(24) Geick, R.; Perry, C. H.; Rupprecht, G. *Phys. Rev.* **1966**, *146*, 543.
(25) Katzir, A.; Suss, J. T.; Zunger, A.; Halperin, A. *Phys. Rev. B* **1975**, *11*, 2370.
(26) Lavrenko, V. A.; Alexeev, A. F. *Ceram. Int.* **1986**, *12*, 25.
(27) Coles, N. G.; Glasson, D. R.; Jayaweera, S. A. A. *J. Appl. Chem.* **1969**, *19*, 178.
(28) Turpin-Launay, D.; Goeuriot, P.; Orange, G.; Thevenot, F.; Fantozzi, G. *Rev. Int. Hautes Temp. Refract.* **1983**, *20*, 147.
(29) Biagioni, R. N. *Chem. Abstr.* **1981**, *95*, 231164.
(30) Hooley, J. G. *Carbon* **1983**, *21*, 181.
(31) Kouvetakis, J.; Kaner, R. B.; Sattler, M. L.; Bartlett, N. *Chem. Commun.* **1986**, 1758. Kaner, R. B.; Kouvetakis, J.; Warble, C. E.; Sattler, M. L.; Bartlett, N. *Mater. Res. Bull.* **1987**, *22*, 399.
(32) Sakamoto, M.; Speck, J. S.; Dresselhaus, M. S. *J. Mater. Res.* **1986**, *1*, 685.
(33) Ishii, T.; Sato, T.; Tanuma, S.; Okabe, K. Jpn. Kokai Tokkyo Koho JP 62,212,205 [87,212,205], 1987; *Chem. Abstr.* **1988**, *108*, 78222s.
(34) Finicle, R. L. *Ind. Res. Dev.* **1983**, *25*, 113.
(35) Steele, J. H.; Engel, R. *Adv. Ceram. Mater.* **1988**, *3*, 452.
(36) Rice, R. W.; Matt, C. V.; McDonough, W. J.; McKinney, K. R.; Wu, C. C. *Ceram. Sci. Eng. Proc.* **1982**, *3*, 698.
(37) Rice, R. W.; Spann, J. R.; Lewis, D.; Coblenz, W. *Ceram. Sci. Eng. Proc.* **1984**, *5*, 614.
(38) Rice, R. W. *Ceram. Sci. Eng. Proc.* **1981**, *2*, 661.
(39) Rossi, R. C. Thermal Shock Resistant Materials. In *Ceramics in Severe Environments*; Kriegel, W. W., Palmour, H., III, Eds.; Plenum Press: New York, 1970; Vol. 5, p 123.
(40) Rossi, R. C.; Carnahan, R. D. U.S Pat. 4,007,049, Feb 8, 1977.
(41) Rice, R. W.; McDonough, W. J.; Freiman, S. W.; Mecholsky, J. J., Jr. U.S. Pat. 4,304,870, Dec 8, 1981.
(42) Lewis, D.; Ingel, R. P.; McDonough, W. J.; Rice, R. W. *Ceram. Eng. Sci. Proc.* **1981**, *2*, 719.
(43) Coblenz, W. S. U.S. Pat. 4,539,300, Sept 3, 1985. Coblenz, W. S.; Lewis, D., III. *J. Am. Ceram. Soc.* **1988**, *71*, 1080.
(44) Murata, Y.; Miccioli, B. R. *Ceram. Bull.* **1970**, *49*, 718.
(45) Economy, J.; Anderson, R. *Inorg. Chem.* **1966**, *5*, 989.
(46) Economy, J.; Anderson, R. V. *Text. Res. J.* **1966**, 36.
(47) Economy, J.; Anderson, R. V. *J. Polym. Sci., Part C* **1967**, *19*, 283.
(48) Lin, R. Y.; Economy, J.; Murty, H. H.; Ohnsorg, R. *Appl. Polym. Symp.* **1976**, *29*, 175. Economy, J. *Ibid.* **1977**, *31*, 23.
(49) Lindemanis, A. E. *Mater. Sci. Res.* **1984**, *17*, 111.
(50) Kazakov, M. E.; Kirilenko, Y. K.; Trushnikov, A. M.; Misin, V. M.; Kalachev, A. I.; Kudryattsev, G. I.; Valetskii, P. M.; Cherkashin, M. I. *Dokl. Akad. Nauk SSSR* **1986**, *287*, 1139.
(51) Rice, R. W. U.S. Pat. Appl. U.S. 700,246, Aug 1985.
(52) Freeman, G. B.; Lackey, W. J.; Starr, T. L. *Proc. Electron Microsc. Soc.* **1988**, 740.
(53) Singh, R. N.; Brun, M. K. *Adv. Ceram. Mater.* **1988**, *3*, 235.
(54) Brun, M. K.; Singh, R. N. *Adv. Ceram. Mater.* **1988**, *3*, 506.
(55) Singh, R. N.; Brun, M. K. *Ceram. Sci. Eng. Proc.* **1987**, *8*, 636.
(56) Ruh, R.; Zangvil, A.; Wills, R. R. *Adv. Ceram. Mater.* **1988**, *3*, 411.
(57) Mazdiyasni, K. S.; Ruh, R. *J. Am. Ceram. Soc.* **1981**, *64*, 415.
(58) Iwasa, M.; Kakiuchi, S. *Yogyo Kyokaishi* **1985**, *93*, 661; *Chem. Abstr.* **1985**, *103*, 182536e.
(59) Hirai, T.; Goto, T.; Sakai, T. *Emergent Process Methods for High Technology Ceramics*; Davis, R. F., Palmour, H., III, Porter, R. L., Eds.; Plenum Press: New York, 1982.
(60) Besmann, T. M. *J. Am. Ceram. Soc.* **1986**, *69*, 69.
(61) Sugiyama, K.; Ohsawa, Y. *J. Mater. Sci. Lett.* **1988**, *7*, 1221.
(62) Mazdiyasni, K. S.; Ruh, R.; Hermes, E. E. *Am. Ceram. Soc. Bull.* **1985**, *64*, 1149.
(63) Kuramoto, N.; Takada, K.; Numata, Y. U.S. Pat. 4,642,298, 1987.
(64) Morris, J. R.; Tangilli, R. A. U.S. Pat. 4,666,873, 1987.
(65) Rice, R. W. Processing Ceramic Composites. In *Ceramic Processing Techniques*; Binner, J. G. P., Ed.; Moyes Publishers: London, in press.
(66) Meller, A. In *Gmelin Handbuch der Anorganische Chemie, Boron Compounds*; Niedenzu, K., Ed.; Springer-Verlag: Berlin, 1980; 1st Suppl., Vol. 2, p 1 and references therein.
(67) Fister, D. *Ceram. Eng. Sci. Proc.* **1985**, *6*, 1305.
(68) Rusanova, L. N.; Romashin, A. G.; Kulikova, G. L.; Golubeva, O. P. *Poroshk. Metall. (Kiev)* **1988**, 23.
(69) Ogasawara, T.; Koshida, T.; Koitabashi, T.; Sasaki, K. Eur. Pat. Appl. EP 170,817, 1986; *Chem. Abstr.* **1986**, *104*, 132430r. Ogasawara, T.; Koshida, T.; Koitabashi, H.; Sasaki, K. *Jpn. Kokai Tokkyo Koho JP* 60,260,405 [85,260,405], 1985; *Chem. Abstr.* **1986**, *105*, 45796s. Ogasawara, T.; Koshida, T.; Sasaki, K. Jpn. Kokai Tokkyo Koho JP 61,256,905 [86,256,905], 1986; *Chem. Abstr.* **1987**, *106*, 87163j.
(70) Brozek, V.; Dufek, V.; Sasak, S. Czech CS 243,889, 1987; *Chem. Abstr.* **1988**, *108*, 61251c.
(71) Shin-Etsu Chemical Industry Co., Ltd. Jpn. Kokai Tokkyo Koko JP 83-140142, 1983; *Chem. Abstr.* **1984**, *100*, 16265.
(72) Komatsu, Ltd. Jpn. Kokai Tokkyo Koko JP 83-60603, 1983; *Chem. Abstr.* **1983**, *99*, 42531.
(73) National Institute for Research of Inorganic Materials Jpn. Kokai Tokkyo JP 83-181708, 1983; *Chem. Abstr.* **1984**, *100*, 24032.
(74) Lornikhov, L. K.; Kornilov, A. A.; Galevskii, G. V.; Perskip, V. D.; Krutskii, Yu. L. *Disp. Kristal. Poroshi., Mater. (Kiev)* **1980**, *52*; *Chem. Abstr.* **1981**, *94*, 6733.
(75) Krutskii, Yu. L.; Kornilov, A. A.; Lamikov, L. K. *Khim. Elektroterm. Plazmorkhim. (Leningrad)* **1980**, 107.
(76) King, E. M. Ger. 1,087,578, 1958; *Chem. Abstr.* **1958**, *52*, 1147*f*.
(77) O'Connor, T. E. *J. Am. Chem. Soc.* **1962**, *84*, 1753.
(78) Gontarz, Z.; Podsiadlo, S. *Pol. J. Chem.* **1984**, *58*, 3. Podsiadlo, S.; Orzel, J. *Ibid.* **1984**, *58*, 323.
(79) Koshida, T.; Ogasawara, T.; Sasaki, K. Jpn. Kokai Tokkyo Koho JP 61 72,606 [8672,606], 1986; *Chem. Abstr.* **1986**, *105*, 81761*k*.
(80) Matsuda, F.; Kato, K. Jpn. Kokai Tokkyo Koho JP 61,111,904 [86,111,904], 1986; *Chem. Abstr.* **1987**, *106*, 20659*g*. Matsuda, F.; Kato, K. Jpn. Kokai Tokkyo Koho JP

61,295,211 [86,295,211], 1986; *Chem. Abstr.* **1987**, *107*, 99238*w*.

(81) Yoshida, Y.; Aoyanagi, K.; Katayama, K.; Iizuka, Y. Jpn. Kokai Tokkyo Koho JP 61,286,207 [86,286,207], 1986; *Chem. Abstr.* **1987**, *106*, 216453*e*.

(82) Gontarz, Z.; Podsiadlo, S. *Pol. J. Chem.* **1984**, *3*, 3, 13. Gontarz, Z.; Orzel, J. *Pol. J. Chem.* **1984**, *3*, 323.

(83) Toshiba Monofax Co. Jpn. Kokai Tokkyo Koho JP 83-41706, 1983; *Chem. Abstr.* **1983**, *99*, 24973.

(84) Huang, Z.; Gao, G.; Suo, Y.; Liu, C. *Runhua Yu Mifeng* **1984**, 45; *Chem. Abstr.* **1985**, *103*, 162610*w*.

(85) National Institute for Research in Inorganic Materials Jpn. Kokai Tokkyo Koho JP 83-181707, 1983; *Chem. Abstr.* **1984**, *100*, 24033.

(86) Troitskii, V. N.; Grebtsov, B. M.; Damashnev, I. A.; Gurov, S. V. *Proc. 1st Annu. Int. Conf. Plasma Chem. Technol., San Diego, 1982* **1983**, 141; *Chem. Abstr.* **1984**, *100*, 202318.

(87) McDonad, J. K.; Warren, L. C.; Merrit, J. A. *Chem. Abstr.* **1982**, *92*, 13556.

(88) Showa Denko, K. K. Jpn. Kokai Tokkyo Koho JP 82-22105, 1982; *Chem. Abstr.* **1982**, *96*, 222229.

(89) Bamberger, C. E.; Begun, G. M. *J. Am. Ceram. Soc.* **1986**, *69*, C-95.

(90) Shin-Etsu Chemical Industry Co. Jpn. Kokai Tokkyo Koho JP 83-140142, 1983; *Chem. Abstr.* **1984**, *100*, 16265.

(91) Messier, R. *Mater. Res. Soc. Bull.* **1988**, *13*, 18; *Ibid.* **1988**, *13*, 29 and companion articles in the same issues.

(92) Stinton, D. P.; Besmann, T. M.; Lowden, R. A. *Ceram. Bull.* **1988**, *67*, 350. Houle, F. A. *Appl. Phys. A* **1986**, *41*, 315. Green, M. L.; Levy, R. A. *J. Met.* **1985**, 63.

(93) Arya, S. P. S.; D'Amico, A. *Thin Solid Films* **1988**, *157*, 267 and references therein.

(94) Takahashi, T.; Itoh, H.; Takeuchi, A. *J. Cryst. Growth* **1979**, *47*, 245.

(95) Sano, M.; Aoki, M. *Thin Solid Films* **1981**, *83*, 247.

(96) Motojima, S.; Tamura, Y.; Sugiyama, K. *Thin Solid Films* **1982**, *88*, 269.

(97) Fukushima, K. Jpn. Kokai Tokkyo Koho JP 62,243,770 [87,243,770], 1987; *Chem. Abstr.* **1988**, *108*, 42845*h*.

(98) Matsuda, T.; Uno, N.; Nakae, H.; Hirai, T. *J. Mater. Sci.* **1986**, *21*, 649.

(99) Hurd, J. L.; Perry, D. L.; Lee, B. T.; Yu, K. M.; Bourret, E. D.; Haller, E. E. *J. Mater. Res.* **1989**, *4*, 350.

(100) Baronian, W. *Mater. Res. Bull.* **1972**, *7*, 119.

(101) Rand, M. J.; Roberts, J. *J. Electrochem. Soc.* **1968**, *115*, 423.

(102) Muraka, S. P.; Chang, C. C.; Wang, D. N. K.; Smith, T. E. *J. Electrochem. Soc.* **1979**, *126*, 1951.

(103) Hirayama, M.; Shohno, K. *J. Electrochem. Soc.* **1975**, *122*, 1671.

(104) Adams, A. C.; Capio, C. D. *J. Electrochem. Soc.* **1980**, *127*, 399.

(105) Adams, A. C. *J. Electrochem. Soc.* **1981**, *128*, 1379.

(106) Dana, S. S.; Maldonado, J. R. *J. Vac. Sci. Technol. B* **1986**, *4*, 235.

(107) Hyder, S. B.; Yep, T. O. *J. Electrochem. Soc.* **1976**, *123*, 1721.

(108) Miyamoto, H.; Hirose, M.; Osaka, Y. *Jpn. J. Appl. Phys.* **1983**, *22*, L216.

(109) Yuzuriha, T. H.; Mlynko, W. E.; Hess, D. W. *J. Vac. Sci. Technol. A* **1985**, *3*, 2135.

(110) Yuzurika, T. H.; Hess, D. W. *Thin Solid Films* **1986**, *140*, 199.

(111) Adams, A. *J. Electrochem. Soc.* **1981**, *128*, 1378.

(112) Savel'ev, A. A.; Pukhov, A. A.; Vishnyakov, B. A.; Sulimin, A. D.; Ischenko, A. P. *Fiz. Khim. Obrab. Mater.* **1981**, 85.

(113) Shanfield, S.; Wolfson, R. *J. Vac. Sci. Technol. A* **1983**, *1*, 323.

(114) Hoshino, Y.; Takase, Y. Jpn. Kokai Tokkyo Koho JP 61,149,478 [86,149,478], 1986; *Chem. Abstr.* **1987**, *106*, 35557*w*.

(115) Constant, G.; Feurer, R. *J. Less-Common Met.* **1981**, *82*, 113.

(116) Schleich, D. M.; Lai, W. Y. F.; Lam, A. *Transformation of Organometallics and Exotic Materials: Design and Activation*; Laine, R. M., Ed.; M. Highoff Publishers: Dordrecht, 1988; p 174.

(117) Nakamura, K. *J. Electrochem. Soc.* **1985**, *132*, 1757.

(118) Montasser, K.; Hattori, S.; Morita, S. *Thin Solid Films* **1984**, *117*, 311.

(119) Grauleau, D.; Shroff, A. *Chem. Abstr.* **1982**, *96*, 27511.

(120) Steinberg, H.; Brotherton, R. J. *Organoboron Chemistry*; Wiley: New York, 1966; Vol. 2.

(121) Reference 3a, p 384 and references therein; ref 3b, p 91 and references therein.

(122) Meller, A. *Top. Curr. Chem.* **1970**, *15*, 146.

(123) Maringgele, W. *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Ed.; Academic Press: London, 1987; Vol. I, p 17.

(124) Gaines, D. F.; Borlin, J. *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975; p 241.

(125) Niedenzu, K.; Dawson, J. W. *Boron-Nitrogen Compounds*; Academic Press: New York, 1965.

(126) Stock, A.; Pohland, E. *Chem. Ber.* **1926**, *59*, 2215.

(127) Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 6084. Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1958**, *80*, 8. Shore, S. G.; Böddeker, K. W. *Inorg. Chem.* **1964**, *3*, 914.

(128) Wiberg, E. *Naturwissenschaften* **1948**, *35*, 182, 212.

(129) Laubengayer, A. W.; Moews, P. C., Jr.; Porter, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 1337.

(130) Mamantov, G.; Margrave, J. L. *J. Inorg. Nucl. Chem.* **1961**, *20*, 348.

(131) Beck, J. S.; Sneddon, L. G., personal communication.

(132) Gasparis-Ebeling, T.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 303.

(133) Neiss, M. A.; Porter, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 1438.

(134) Porter, R. F.; Turbini, L. J. *Top. Curr. Chem.* **1981**, *96*, 1.

(135) Simonson, J.; Paffett, M. T.; Paine, R. T. *J. Vac. Soc.*, submitted.

(136) Hirano, S.; Naka, S. Jpn. Kokai Tokkyo Koho JP 61,117,107 [86,117,107] 1986. Hirano, S.; Yogo, T.; Asada, S.; Naka, S. *J. Am. Ceram. Soc.* **1989**, *72*, 66.

(137) Toeniskoetter, R. H.; Hall, F. R. *Inorg. Chem.* **1963**, *2*, 29.

(138) Hu, M. G.; Van Paasschen, J. M.; Geanangle, R. A. *J. Inorg. Nucl. Chem.* **1977**, *39*, 2147. Hu, M. G.; Geanangle, R. A.; Wendlandt, W. W. *Thermochim. Acta* **1978**, *23*, 249. Komm, R.; Geanangle, R. A.; Liepins, R. *Inorg. Chem.* **1983**, *22*, 1684. Sit, V.; Geanangle, R. A.; Wendlandt, W. W. *Thermochim. Acta* **1987**, *113*, 379.

(139) This insoluble, white solid has presumably been isolated from a variety of reactions performed in several laboratories, and these observations are summarized in ref 120, p 342. The material has never been properly characterized due to its insolubility in common organic solvents and its thermal sensitivity.

(140) Dahl, G. H.; Schaeffer, R. *J. Am. Chem. Soc.* **1961**, *83*, 3032.

(141) Beck, J. S.; Albani, C. R.; McGhie, A. R.; Rothman, J. B.; Sneddon, L. G. *Chem. Mater.* **1989**, *1*, 433.

(142) Yogo, T.; Matsuo, S.; Naka, S. *Yogyo Kyokaishi* **1987**, *95*, 94; *Chem. Abstr.* **1987**, *106*, 106650*j*.

(143) Polushin, N. I.; Burdina, K. P. *Chem. Abstr.* **1984**, *101*, 239374*r*.

(144) Aldinger, F.; Kalz, H.-J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 371.

(145) Richerson, D. W. *Modern Ceramic Engineering: Properties, Processing and Use in Design*; Marcel Dekker: New York, 1982.

(146) Auxiliaries refer to those agents that may be added to a ceramic powder to aid in handling and processing the powder into a green body and finally a finished ceramic.[144] A variety of organic polymers are typically employed as auxiliaries, and these are removed in the final pyrolysis processing stages. A green body is the material formed from combination of ceramic powder, auxiliaries, and sintering additives and pressed into a desired shape.[1,144]

(147) Jenkins, G. M.; Kawamura, K. *Polymeric Carbon–Carbon Fibre, Glass and Char*; Cambridge University Press: London, 1976.

(148) Ainger, F. W.; Herbert, J. M. *The Preparation of Phosphorus–Nitrogen Compounds as Non-Porous Solids, Special Ceramics 1960*; Popper, P., Ed.; Academic Press: New York, 1960; p 168.

(149) Chantrell, P. G.; Popper, P. *Inorganic Polymers and Ceramics, Special Ceramics 1964*. Popper, P. *New Electrical Ceramics and Inorganic Polymers, Brit. Ceram. Res. Assn. Spec. Publ. 57*, **1967**.

(150) Verbeek, W. U.S. Pat. 3,853,567, 1974. Winter, G.; Verbeek, W.; Mausmann, M. U.S. Pat. 3,892,583, 1975.

(151) Mazdyasni, K. S.; West, R.; David, L. D.; Djurovich, P. I.; Stearley, K. L.; Srinivasan, K. S. V.; Yu, H. *J. Am. Chem. Soc.* **1981**, *103*, 7352. West, R.; Maxka, J. *ACS Symp. Ser.* **1988**, *No. 360*, 6.

(152) Yajima, S.; Hasegawa, Y.; Okamura, K.; Matsuzawa, T. *Nature* **1978**, *273*, 525. Yajima, S.; Okamura, K.; Hayashi, J.; Omori, M. *J. Am. Ceram. Soc.* **1976**, *59*, 324.

(153) Taniguchi, I.; Harada, K.; Maeda, T. Jpn. Kokai Tokkyo Koho 7,653,000 [76,653,000], 1975; *Chem. Abstr.* **1976**, *85*, 96582*v*.

(154) Rice, R. W.; Wynne, K. J.; Fox, W. B. U.S. Pat. 4,097,294, 1978.

(155) Rice, R. W. *Am. Ceram. Soc. Bull.* **1983**, *62*, 889.

(156) Walker, B. E., Jr.; Rice, R. W.; Becker, P. F.; Bender, B. A.; Coblenz, W. S. *Am. Ceram. Soc. Bull.* **1983**, *62*, 916.

(157) Wynne, K. J.; Rice, R. *Annu. Rev. Mater. Sci.* **1984**, *14*, 297.

(158) Seyferth, D. *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*; Laine, R. M., Ed.; M. Nijhoff Publishers: Dordrecht, 1988; p 133.

(159) Lappert, M. F. *Developments in Inorganic Polymer Chemistry*; Lappert, M. F., Leigh, G. J., Eds.; Elsevier: Amsterdam, 1962; p 20.

(160) Wada, H.; Ito, S.; Kuroda, K.; Kato, C. *Chem. Lett.* **1985**, 691.

(161) Wada, H.; Nojima, K.; Kuroda, K.; Kato, C. *Yogyo Kyosaishi* **1987**, *95*, 130; *Chem. Abstr.* **1987**, *106*, 89061*y*.

(162) Burch, J. E.; Gerrard, W.; Mooney, E. F. *J. Chem. Soc.* **1962**, 2200. See also ref 120, pp 453–457 and references therein.

(163) Shaw, S. Y.; DuBois, D. A.; Neilson, R. H. *ACS Symp. Ser.* **1980**, *No. 360*, 385. Shaw, S. Y.; DuBois, D. A.; Watson, W. H.; Neilson, R. H. *Inorg. Chem.* **1988**, *27*, 974.

(164) Maya, L. *J. Electrochem. Soc.* **1988**, *135*, 1278. Maya, L. *J. Am. Ceram. Soc.* **1988**, *71*, 1104.

(165) Johnson, R. E. U.S. Pat. 4,810,436, Mar 7, 1989.

(166) Rees, W. S., Jr.; Seyferth, D. *J. Am. Ceram. Soc.* **1988**, *71*, C194. Seyferth, D.; Rees, W. S., Jr.; Haggerty, J. S.; Lightfoot, A. *Chem. Mater.* **1989**, *1*, 45. Rees, W. S., Jr.; Seyferth, D. *Ceram. Eng. Sci. Proc.* **1988**, *9*, 1009. Lightfoot, A.; Rees, W. S., Jr.; Haggerty, J. S. *Ibid.* **1988**, *9*, 1021.

(167) Cragg, R. H.; Fortain, M. S.; Greenwood, N. N. *J. Chem. Soc. A* **1970**, 1817. Adams, R. M. *Boron, Metalloboron Compounds and Boranes*; Wiley: New York, 1964. Shore, S. G. *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975. Burg, A. B. *Chem. Soc., Spec. Publ.* **1961**, *No. 15*, 17.

(168) Mirabelli, M. G. L.; Sneddon, L. G. *J. Am. Chem. Soc.* **1988**, *110*, 3305.

(169) Mirabelli, M. G. L.; Sneddon, L. G. *Inorg. Chem.* **1988**, *27*, 3271. Mirabelli, M. G. L.; Lynch, A. T.; Sneddon, L. G. *Solid State Ionics* **1988**, *32/33*, 655.

(170) Wagner, R. I.; Bradford, J. L. *Inorg. Chem.* **1962**, *1*, 99. Wagner, R. I. U.S. Pat. 3,288,726, 1966; *Chem. Abstr.* **1967**, *66*, 38349*w*.

(171) Gerrard, W.; Hudson, H. R.; Mooney, E. F. *J. Chem. Soc.* **1962**, 113.

(172) Lappert, M. F. *Proc. Chem. Soc.* **1959**, 59. Lappert, M. F.; Majunder, M. K. *Proc. Chem. Soc.* **1961**, 425. Aubrey, D. W.; Lappert, M. F. *J. Chem. Soc.* **1959**, 2927.

(173) Seyferth, D.; Kögler, H. P. *J. Inorg. Nucl. Chem.* **1960**, *15*, 99.

(174) Gutmann, V.; Meller, A.; Schlegel, R. *Monatsh. Chem.* **1964**, *95*, 314.

(175) Larcombe, B. E.; Turner, H. S. *Chem. Ind. (London)* **1963**, 410.

(176) Toeniskoetter, R. H.; Killip, K. A. *J. Am. Chem. Soc.* **1964**, *86*, 690.

(177) Bartlett, R. K.; Turner, H. S.; Warne, R. J.; Young, M. A.; MacDonald, W. S. *Proc. Chem. Soc.* **1962**, 153.

(178) Korshak, V. V.; Zamyatna, V. A.; Oganesyan, R. M. *Bull. Akad. Sci. USSR (Div. Chem. Sci.)* **1962**, 1754.

(179) Mikhailov, B. M.; Galkin, A. F. *Bull. Akad. Sci. USSR (Div. Chem. Sci.)* **1963**, 575.

(180) Gerrard, W. *Chem. Ind. (London)* **1961**, *No. 13*, 328. Gerrard, W.; Mooney, E. F.; Rothenburg, R. A. *J. Appl. Chem.* **1962**, *12*, 373.

(181) Niedenzu, K.; Dawson, J. W. *Angew. Chem.* **1960**, *72*, 920.

(182) Korshak, V. V.; Zamyatina, V. A.; Oganesyan, R. M. *Bull. Akad. Sci. USSR (Div. Chem. Sci.)* **1962**, 1580.

(183) Korshak, V. V.; Sosin, S. L.; Alekseeva, V. P. *Proc. Akad. Sci. USSR (Chem. Sect.)* **1960**, *132*, 517.

(184) Toeniskoetter, R. H.; Didchenko, R. Can. Pat. 685,580, 1964.

(185) Gutmann, V. A.; Meller, A.; Schlegel, R. *Monatsh. Chem.* **1963**, *94*, 733.

(186) Meller, A.; Füllgrabe, H.-J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 359.

(187) Meller, A.; Füllgrabe, H.-J. *Z. Naturforsch. B* **1978**, *33B*, 156.

(188) Meller, A.; Füllgrabe, H.-J. *Chem. Ber.* **1978**, *111*, 819.

(189) Meller, A.; Füllgrabe, H.-J.; Habben, C. D. *Chem. Ber.* **1979**, *112*, 1252.

(190) Taniguchi, I.; Harada, K.; Maeda, T. Jpn. Kokai Tokkyo 76 53,000, 1976; *Chem. Abstr.* **1976**, *85*, 96582*v*.

(191) Taniguchi, I.; Kimura, Y.; Yamamoto, K. Ger. Offen. DE 3,528,394, 1986; *Chem. Abstr.* **1986**, *105*, 134537*a*.

(192) Paciorek, K. J. L.; Kratzer, R. H.; Harris, D. H.; Smythe, M. E. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1984**, *25*, 15.

(193) Paciorek, K. J. L.; Harris, D. A.; Kratzer, R. H.; Smythe, M. E.; Kimble, P. F. Report SN-2022-F, 1985 (Order No. AD-A158658); *Chem. Abstr.* **1986**, *104*, 211726*v*.

(194) Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.* **1987**, *109*, 5867. Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.*, in press.

(195) Blum, Y. D.; Laine, R. M. U.S. Pat. 4,801,439, 1989.

(196) Paciorek, K. J. L.; Kratzer, R. H.; Harris, D. H.; Smythe, M. E.; Kimble, P. F. U.S. Pat. 4,581,468, 1986.

(197) Paciorek, K. J. L.; Harris, D. A.; Kratzer, R. H. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 173.

(198) Paciorek, K. J. L.; Krone-Schmidt, W.; Harris, D. H.; Kratzer, R. H.; Wynne, K. J. *ACS Symp. Ser.* **1988**, *No. 360*, 392.

(199) Paciorek, K. J. L.; Kratzer, R. H. *Ceram. Eng. Sci. Proc.* **1988**, *9*, 993.

(200) Paciorek, K. J. L.; Kratzer, R. H.; Harris, D. H.; Krone-Schmidt, W. U.S. Pat. 4,707,556, **1987**.

(201) Bender, B. A.; Rice, R.; Spann, J. R. *Ceram. Eng. Sci. Proc.* **1985**, *6*, 1171.

(202) Bender, B. A.; Rice, R.; Spann, J. R. *J. Am. Ceram. Soc.* **1987**, *70*, C-58.

(203) Paciorek, K. J. L.; Kratzer, R. H.; Kimble, P. F.; Nakahara, J. H.; Wynne, K. J.; Day, C. S. *Inorg. Chem.* **1988**, *27*, 2432.

(204) Wynne, K. J. *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*; Laine, R. M., Ed.; M. Nijhoff Publishers: Dordrecht, 1988; p 89.

(205) Brinker, C. J.; Clark, D. E.; Ulrich, D. R., Eds. *Better Ceramics through ChemistryI, Proc. Mater. Res. Soc.* **1984**, *32*, 19.

(206) Nöth, H. *Z. Naturforsch.* **1961**, *16B*, 618.

(207) Narula, C. K.; Paine, R. T.; Schaeffer, R. *Proc. Mater. Res. Soc.* **1986**, *73*, 383.

(208) Narula, C. K.; Paine, R. T.; Schaeffer, R. *ACS Symp. Ser.* **1988**, *No. 360*, 378.

(209) Narula, C. K.; Lindquist, D. A.; Fan, M. M.; Borek, T. T.; Duesler, E. N.; Datye, A. K.; Schaeffer, R.; Datye, A. K.; Schaeffer, R.; Paine, R. T. *Chem. Mater.*, submitted.

(210) Huffman, J. C.; Füsstetter, H.; Nöth, H. *Z. Naturforsch.* **1976**, *31B*, 289. Hess, H.; Reiser, B. *Z. Anorg. Allg. Chem.* **1971**, *381*, 91.

(211) Harshbarger, W.; Lee, G. H.; Porter, R. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1969**, *91*, 551.

(212) Narula, C. K.; Schaeffer, R.; Datye, A. K.; Borek, T. T.; Paine, R. T. *Chem. Mater.*, submitted.

(213) Beachley, O. T.; Durkin, T. R. *Inorg. Chem.* **1974**, *13*, 1768.

(214) Narula, C. K.; Schaeffer, R.; Paine, R. T.; Datye, A. K.; Hammetter, W. F. *J. Am. Chem. Soc.* **1987**, *109*, 5556.

(215) Rye, R. R.; Borek, T. T.; Lindquist, D. A.; Paine, R. T. *J. Am. Ceram. Soc.*, submitted.

(216) Paine, R. T.; Narula, C. K.; Schaeffer, R.; Datye, A. K. *Chem. Mater.* **1989**, *1*, 486.

(217) Datye, A. K.; Paine, R. T.; Narula, C. K.; Allard, L. *Proc. Mater. Res. Soc.*, accepted.

(218) Lindquist, D. A.; Datye, A. K.; Paine, R. T., to be published.

(219) Paine, R. T.; Narula, C. K.; Schaeffer, R.; Lindquist, D. A.; Borek, T. T. U.S. Pat. Appl. 07/312,956, Feb 17, 1989. Paine, R. T.; Narula, C. K.; Schaeffer, R. U.S. Pat. Appl. 07/312,881, Feb 17, 1989.

(220) Gesser, H. D.; Goswami, P. C. *Chem. Rev.* **1989**, *89*, 765.

(221) Lindquist, D. A.; Borek, T. T.; Kramer, S. J.; Narula, C. K.; Johnston, G.; Schaeffer, R.; Smith, D. M.; Paine, R. T. *J. Am. Ceram. Soc.*, submitted.

(222) Clēment, R.; Proux, Y. *Bull. Soc. Chim. Fr.* **1969**, 558.

(223) Niedenzu, K.; Dawson, J. W. *J. Am. Chem. Soc.* **1959**, *81*, 3561; *Angew. Chem.* **1961**, *73*, 433.

(224) Mikhailov, B. M.; Galkin, A. F. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1961**, 345.

(225) Narula, C. K.; Schaeffer, R.; Paine, R. T.; Datye, A. K. *Inorg. Chem.* **1989**, *28*, 4053.