change in morphology was related to surface smoothness. However, polishing had little or no effect on the morphological distribution of crystals from either the cleaned or uncleaned electrodes. One final point worth noting regarding the data in Table I is that all of the crystals grown on the graphite electrodes (α or β) took less time to start growing (overnight versus 2–3 days) and required lower current densities (0.8 $\mu A/cm^2$ versus 1.5 $\mu A/cm^2$) than is typical for platinum electrode syntheses.

The observed phase selectivity by use of treated and untreated graphite electrodes prompted us to perform several comparative electrochemical (platinum anodes) and chemical syntheses of $(ET)_2I_3$ (Table II). The selectivity is most likely associated with a chemical change in the graphite electrodes upon electrolysis. Anodic oxidation of graphite in sulfuric acid solution forms graphite–bisulfate, $C_{24n}{}^{+}HSO_4{}^{-}\cdot 2.5H_2SO_4$, where n is the stage number.[10] For n equal to 1 or 2, the materials are well characterized and correspond to sulfuric acid–bisulfate intercalation between every carbon layer or every two carbon layers, respectively. Under the "cleaning" conditions of the experiments in Table I, the graphite electrodes are incompletely oxidized, i.e., n equals a large number. Even so, the treated electrodes can easily take up a substantial amount of sulfuric acid. For example, with a low average state of oxidation, e.g., $n = 100$, a graphite electrode would contain 60 mol % of sulfuric acid relative to the organic heterocyclic component. The first entry in Table II provides typical experimental conditions and results for $(ET)_2I_3$ syntheses using platinum electrodes. The second shows the effect of adding a small amount of sulfuric acid. Crystal growth occurs at lower current densities, and less time is required for nucleation. The yield of $(ET)_2I_3$ is comparable to what is observed under the standard conditions, but now the α phase constitutes 25% of the products. Accordingly, sulfuric acid can significantly influence which morphology is produced. However, so can water. When 4 mol % of water is added, only 9% of the products is the β phase. This is an interesting observation, since water is usually rigorously excluded in $(ET)_2I_3$ preparations. Adding an alternative oxidant, such as aqueous hydrogen peroxide, gives crystals that are exclusively the α phase. Apparently, a variety of additives are capable of facilitating α-phase growth. The final electrocrystallization result in Table II illustrates what happens when the current density is increased substantially: the product is mainly the α phase and microcrystalline. It has been noted previously that rapid crystal growth at high current densities favors the formation of α-$(ET)_2I_3$.[15,16] Rapid crystal growth (1 h) is probably responsible for the formation of large amounts of α product in the chemical oxidations also. The room-temperature electrical conductivity of the α-phase crystals is greater than those of the β phase [$\sigma_{300}(\alpha \text{ phase}) = 60\text{–}250$ S/cm, $\sigma_{300}(\beta \text{ phase}) = 30$ S/cm].[15,16] It is conceivable that the higher conductivity of the α form plays a key role[17] in making α-$(ET)_2I_3$ the kinetically favored product under conditions of rapid crystal growth. It is noteworthy in this regard that α-$(ET)_2I_3$ is thermodynamically less stable than β-$(ET)_2I_3$.[18] Although the results in Table II do not provide an unambiguous picture of how the cleaned graphite electrodes produce the α form almost exclusively, they are highly compatible with the idea that intercalated sulfuric acid and/or associated water are responsible.

As a final test of our findings, crystals of the organic superconductor κ-$(ET)_2Cu(NCS)_2$ have also been prepared by use of graphite anodes. Although at least two other structural modifications of $(ET)_2Cu(NCS)_2$ are known,[19] only the κ phase has formed on either cleaned or uncleaned electrodes. Rf penetration depth measurements yielded $T_c = 10.2 \pm 0.1$ K for graphite-grown κ-$(ET)_2Cu(NCS)_2$.

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Formation of Boron Nitride Coatings on Metal Oxides

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In the past, thin films of ceramic materials including boron nitride have been prepared primarily by vapor deposition techniques.[1] These films are adequate for some applications; however, they vary a great deal in quality and purity.[2] To achieve several advanced materials goals that

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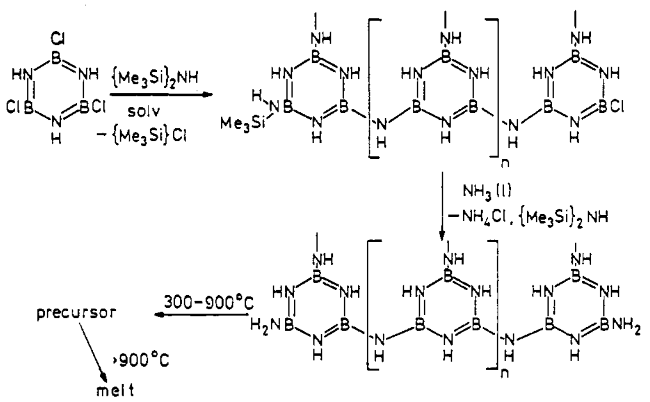
involve BN, it is necessary to develop new methods for forming both thin and thick coatings of highly crystalline h-BN and c-BN modifications on various substrates. As an alternative to vapor deposition, it is shown that some ceramic powders and fibers may be prepared by pyrolysis of selected inorganic polymers.[3] On the other hand, few attempts have been reported on formation of ceramic films from polymeric precursors. Specifically, Taniguchi and co-workers[4] briefly reported that heating *B*-triamino-*N*-triphenylborazene ($[H_2NBN(C_6H_5)]_3$) resulted in a low-temperature melt, and they claimed formation of boron nitride fibers and a film. Further, Paciorek and co-workers[5] noted that heating *B*-triamino-*N*-trisilylborazene ($[H_2NBN(SiR_3)]_3$) produced a melt at low temperature. This material was spun into green fibers and subsequently pyrolyzed in NH_3, leaving carbon-free boron nitride fibers. Paciorek also reported formation of a polymer ($[(Me_3SiN(H)B)_2(BN(H))(NH)_3]_n$) that was soluble in hexane and was used to coat Al_2O_3 fibers.[5] In a different approach, Seyferth and co-workers[6] have recently formed fibers from a polymer based upon decaborane(12)–diamine complexes. Lastly, Sneddon and co-workers[7] have discovered that coatings of BN may be prepared from a precursor obtained from $HBBr_2{\cdot}SMe_2$ and ammonia.

We have previously reported that pyrolysis of solid polymers formed by cross-linking chloroborazenes with hexamethyldisilazane leads to formation of carbon-free h-BN powder.[8] During these studies, we also found simple conditions that permit deposition of dense, highly crystalline films of h-BN on several important oxide substrates, and that chemistry is described here.

In a fashion similar to that described previously,[8] trichloroborazene (37 g, 201 mmol) was dissolved in dry diethyl ether (350 mL), and the solution was cooled to −78 °C. Hexamethyldisilazane (48.7 g, 302 mmol) was added in one portion, the contents were briefly mixed, and the solution was warmed to 25 °C. After 30 min at 25 °C, the volatiles were removed in vacuo. Departing from our previous procedures, the reaction flask was fitted with a dry-ice condenser, and excess dry NH_3 was condensed into the vessel. The resulting colorless solution was allowed to slowly evaporate, leaving a foamy, moisture-sensitive solid (26 g) which was dried in vacuo. Thermal gravimetric analysis of the solid in Ar showed a marked weight loss (42%) between 25 and 300 °C and essentially no further weight loss between 300 and 1100 °C. Large samples of the foamy solid were pyrolyzed in vacuo in a Pt crucible at 900 °C, leaving an amorphous white solid (15.6 g). Off-gases were collected and identified as primarily NH_3 and small amounts of NH_4Cl. A portion of this solid was further pyrolyzed at 1200 °C for 12 h, and powder X-ray diffraction analysis revealed the formation of crystalline h-BN.[9] During the course of this heating, it was noted that the precursor melted at a temperature above 900 °C, and this suggested the possibility of using the precursor as an unprecedented high-temperature melt-coating reagent.

Scheme I[a]



[a] The compound called *B*-trichloroborazene and shown with double bonds is systematically named 2,4,6-trichloroborazine and drawn without double bonds.

Indeed, when the powdered solid precursor was simply physically applied on several oxide substrates including Al_2O_3, TiO_2, and MgO and the mixture heated, a tough, adhering film of h-BN formed on the substrates. To study this process more thoroughly, a sample of the precursor (0.06 g) was physically mixed with well-characterized single crystals (0.06 g) of MgO,[10] and the mixture was heated for 12 h at 1200 °C under nitrogen in a Pt crucible. The resulting crystallites were examined by transmission electron microscopy, and a typical micrograph is shown in Figure 1. An electron diffraction pattern obtained from this sample shows sharp diffraction spots due to the MgO crystals and a diffuse diffraction ring corresponding to the polycrystalline h-BN coating. The lattice spacings agree with those in the literature:[8,10] MgO(002) $d = 0.21$ nm and BN(002) $d = 0.33$ nm. It is apparent that the polymeric precursor melts, nicely wets the surface of the MgO crystallites, and subsequently deposits a relatively uniform, surface-conforming film of h-BN. The micrograph clearly reveals an intimate interface between the BN layers and the MgO, and the film is free of "blow holes" typical of many classically prepared ceramic films. This favorable condition appears since the majority of the gas-evolution chemistry occurs during the preparation of the precursor prior to melt coating. Higher resolution TEM analysis[11] shows that the BN films grows with the basal planes (0001) locally parallel to the surface of the oxide in every instance. This orientational preference may result from bonding of the boron atoms with oxygen atoms on the surface of the substrate.

In our previous studies on the cross-linking of trichloroborazene ($(ClBNH)_3$) with hexamethyldisilazane ($[(CH_3)_3Si]_2NH$), we observed the formation of oligomeric poly(borazinylamine) gels from several organic solvents including chlorobenzene, methylene chloride, and diethyl ether. When the gels were vacuum dried at 25 °C, the resulting solid polymers were insoluble in common organic

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(2) In particular, the crystallinity of films prepared by chemical vapor deposition techniques varies considerably and, as a result, so also does the chemical stability of BN.

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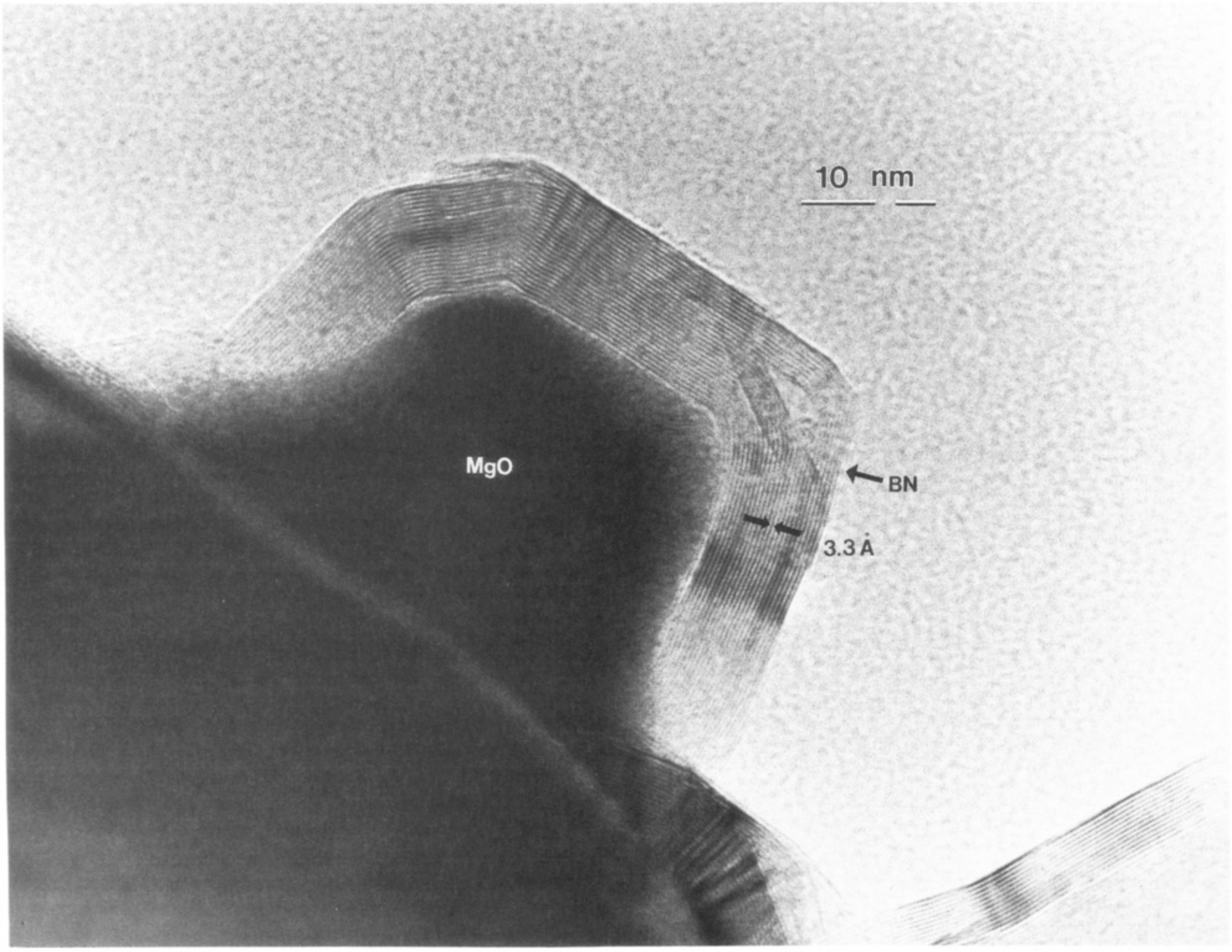

Figure 1. Transmission electron micrograph of h-BN deposited on single-crystal MgO.

solvents, and they were infusible. Polymers prepared in that fashion also retained residual organic solvent as well as small amounts of silicon and chlorine from end-capping groups. Subsequent pyrolysis of the polymers produced only h-BN powder, but if pyrolysis conditions and chemistry were not carefully controlled, the powders retained carbon, chlorine, and silica impurities.

The insolubility, infusibility, and processing impurities have, until now, limited the utility of poly(borazinylamine)s as ceramic precursors for films and fibers. However, the observations presented here offer significant new benefits. In particular, liquid ammonia promotes solvolysis of the undesirable $Me_3SiN(H)$ and Cl end-capping groups present in the gel. Although the full details of the reaction chemistry have not yet been clarified, small quantities of NH_4Cl and $(Me_3Si)_2NH$ are found in the foamy residue isolated from the aminolysis reaction. A general outline of the chemistry is given in Scheme I. The solvolysis chemistry is not unexpected since several investigators have previously reported amination of monomeric borazenes containing halide or organoamine functional groups with subsequent formation of aminoborazenes that tend to undergo subsequent deamination and condensation.[12,13] Indeed, the aminolysis of $(Me_2NBNH)_3$ produces a preceramic polymer that may be converted to h-BN with high yield.[14] EDS analysis of the foamy solid before and after pyrolysis at 900 °C shows the absence of both chlorine and silicon. This contrasts with results of EDS analysis on pyrolyzed samples of poly(borazinylamine)s that have not been exposed to ammonia.[8]

The most significant observation centers on the high-temperature fusibility of the polymer obtained after pyrolysis in the range 300–900 °C. Poly(borazinylamine)s processed by other schemes have not previously been reported to display melting behavior. The structural and mechanistic features that result in this unexpected melting characteristic are not yet understood; however, detailed studies of the melt and the wetting and deposition process on oxide and nonoxide ceramics are in progress. The properties of the coatings indicate that this process holds considerable advantage over vapor deposition techniques if crystalline films are required on a substrate. In addition, the ammonia solutions of the poly(borazinylamine)s offer other processing advantages. For example, we have successfully dip-coated substrates and drawn green fibers from the poly(borazinylamine)/ammonia solution, and these materials have been converted to boron nitride coatings and fibers, respectively.[15]

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Synthesis of Polyoxometalate-Pillared Layered Double Hydroxides via Calcined Precursors

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Layered double hydroxides (LDHs) represent an important group of solids.[1–6] They consist of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules[1,2,7,8] and are, therefore, mirror images of the much studied family of cationic clay minerals.[2] They may be represented by the general formula

$$M^{2+}{}_aM^{3+}{}_b(OH)_{2a+2b}(X^-)_b\cdot xH_2O$$

where M^{2+} may be Mg, Ni, Co, Zn, or Cu and M^{3+} may be Al, Cr, or Fe. M^{2+}/M^{3+} ratios between 1 and 5 are possible.[4,9] Such LDHs have attracted attention as precursors for the generation of solid base catalysts[4,10] as well as being intermediates in the synthesis of more conventional catalysts, e.g., in the formation of copper/cobalt bimetallic catalysts supported on ZnO.[5]

Cl^-, OH^-, and $CO_3{}^{2-}$ are frequently cited as the charge-balancing anions, although recent attempts have aimed at incorporating other guests, for example, $[V_{10}O_{28}]^{6-}$ and α–ω-carboxylic acids (see ref 3 and 6). The high charge densities associated with LDHs, however, suggest that there may be some difficulty in intercalating such large species. Consequently two strategies have been described. The first strategy makes use of the fact that Cl^- or $NO_3{}^-$ anions are significantly easier to displace than, for example, $CO_3{}^{2-}$;[11] for this reason Kwon et al.[3] and Woltermann[12] made use of the Cl^- and $NO_3{}^-$ forms, respectively, in their studies. The second strategy has relied upon an approach whereby the LDH is initially synthesized with a large organic anion (typically the terephthalate dianion) as the intercalated species.[6]

Here we present a third and a particularly straightforward procedure for synthesizing polyoxometalate-pillared LDHs that requires only direct exposure of a calcined precursor to a solution of the pillaring species, i.e., $[V_{10}O_{28}]^{6-}$ or $[Mo_7O_{24}]^{6-}$. Our previous work in this area has concentrated on inserting organic molecules into LDHs.[13] Regeneration of the original LDH structure (typically hydrotalcite) by hydration of the calcined material in carbonated water has been reported elsewhere.[13–18]

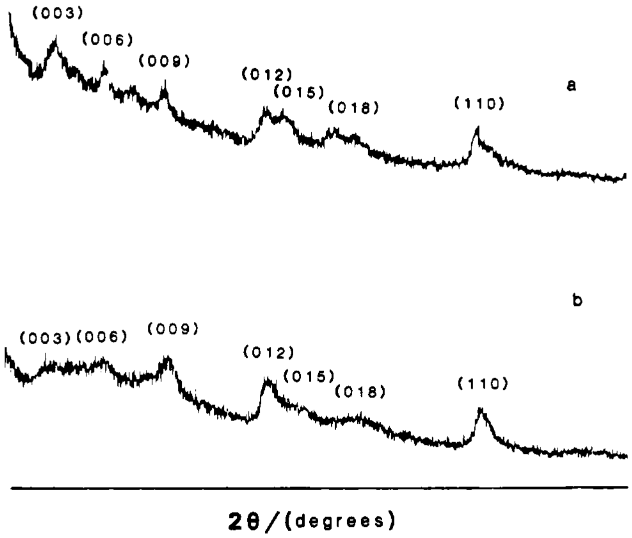

Figure 1. X-ray powder diffraction patterns of (a) Mg–Al–$V_{10}O_{28}$ (d = 11.8 Å) and (b) Mg–Al–Mo_7O_{24} (d = 12.0 Å) prepared via calcined precursor. Miller indices are shown.

Synthesis of the parent LDH followed closely the method of Reichle.[4] A typical composition for the starting material was $Mg_6Al_{3.3}(OH)_{18.6}(CO_3)_{1.7}\cdot 4H_2O$. The LDH was then calcined in air at 450 ± 10 °C for 18 h prior to the following treatments:

$V_{10}O_{28}$-Pillared Mg–Al LDH: 0.2 g of calcined Mg–Al LDH powder and 0.3 g of $NaVO_3$ were added to 10 mL of decarbonated deionized water at room temperature. The mixture was stirred for 10–15 min before the addition of 2 M HCl dropwise with vigorous stirring (acid was added until the pH dropped to 4.5). The pH was observed to drop from 8.8 to 4.5 and maintained at 4.5 for 20–25 min. The products were then filtered and washed thoroughly with hot deionized water. The resulting yellow product was allowed to partially dry under N_2 before further drying in an oven at 110 °C overnight. The product gave a powder X-ray diffraction pattern indicative of a regenerated layered double hydroxide in expanded form,[19] an observation similar to that of the intercalation of organic species.[13] A basal spacing (d_{003}) of 11.8 Å was observed (Figure 1a). Acidification of the calcined LDH in the presence of $NaVO_3$ results in the oligomerization of the metavanadate to form the polyvanadate, and it is this species that is believed to be intercalated. The observed basal spacing is in good agreement with previously reported values of 11.9 and 11.8 Å and corresponds to gallery heights of 7.0 Å and to a $V_{10}O_{28}{}^{6-}$ orientation in which the C_2 axis is parallel to the host layers.[3,6] The observed reflections

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