3210 *Inorg. Chem.* **1994,** *33,* 3210–3211

# Rapid Solid-State-Precursor Synthesis of Crystalline Boron Nitride

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*Received January 4, 1994*

A major concern for solid-state chemistry is minimization of diffusion barriers.[1] Rapid solid-state-precursor synthesis provides a unique approach to push solid reactivity to its limit by performing highly exothermic reactions in a self-sustaining mode.[2] During these reactions, diffusion barriers are significantly reduced because of the facile decomposition of precursors and the formation of molten salts. Consequently, this approach has proven very effective in rapid preparation of several crystalline products including layered transition metal dichalcogenides, transition metal nitrides, and III–V semiconductors.[2–5] Along these lines, some well-known materials that are difficult to crystallize, such as boron nitride, should be accessible. To achieve this goal, an understanding of solid reactivity and reaction kinetics in self-propagating reactions is useful. Because of the presence of high activation energy barriers, highly exothermic reactions do not necessarily self-propagate and/or form crystalline products. For example, the industrial preparation of layered-form hexagonal (h-) BN, $3CaB_6 + B_2O_3 + 10N_2 \rightarrow 20BN + 3CaO$, is highly exothermic (thermodynamically estimated adiabatic temperature $T_{ad} \approx 3400$ °C[6]), but high temperature heating (>1500 °C) is required to obtain h-BN from this reaction.[7] Even explosive reactions such as that found recently between cesium and *B*-trichloroborazine lead to amorphous rather than crystalline BN products.[8] The conversion of disordered turbostratic (t-) BN to its highly ordered relative h-BN must be performed at temperatures >1800 °C in the presence of catalysts.[9] Under typical laboratory synthetic conditions, amorphous BN is obtained along with turbostratic modifications.[10] Here we show that by selecting an appropriate self-sustaining reaction route that avoids energy barriers inherent in conventional approaches, highly **crystalline** boron nitride can be synthesized within seconds with little outside energy input.

Two or twenty millimoles of $MBF_4$ (M = Li, Na, K) and stoichiometric amounts of $Li_3N$ and/or $NaN_3$[11a] are ground together and ignited locally with a resistively heated nichrome wire ($T \leq 850$ °C, time ≈ 1 s). The reactions (Table 1) are self-propagating and go to completion within seconds after ignition. X-ray diffraction (XRD)[12] shows the presence of alkali fluorides (in unwashed products) and boron nitride (in both unwashed and washed products), suggesting the following reaction scheme:

$$MBF_4 + xLi_3N + 3(1-x)NaN_3 \rightarrow BN + MF + 3xLiF + 3(1-x)NaF + 4(1-x)N_2 \quad (1)$$

**Table 1.** Summary of BN Syntheses

| reactions | $-\Delta H^a$ (kJ) | $T_{ad}^{a,b}$ (K) | washed products (yield[c]) |
|---|---|---|---|
| 1. $LiBF_4 + Li_3N$ | 714 | 1954 | t-BN (25%) |
| 2. $NaBF_4 + Li_3N$ | 668 | 1954 (2150) | t-BN (66/**70%**) |
| 3. $KBF_4 + Li_3N$ | 623 | 1783 | t-BN (68%) |
| 4. $LiBF_4 + 3NaN_3$ | 820 | 1954 | does not propagate |
| 5. $NaBF_4 + 3NaN_3$ | 774 | 1850 (1993) | t-BN (45/**70%**) |
| 6. $KBF_4 + 3NaN_3$ | 728 | 1744 | t-BN (55%) |
| 7. $LiBF_4 + 0.8Li_3N + 0.6NaN_3$ | 735 | 1954 | h- + r-BN (**55%**)[e] |
| 8. $NaBF_4 + xLi_3N + 3(1-x)NaN_3$[d] | 714–676 | 1954 | h- + r-BN (**79–84%**)[f] |
| 9. $BI_3 + Li_3N$ | 692 | 1443 | does not propagate |

[a] Calculated on the basis of eq 1 using data from refs 6b and 18. [b] Calculated with constant-pressure (or constant-volume) assumptions. [c] Total chemical yield for 2-mmol reactions and/or for 20-mmol reactions (in **boldface**). [d] $x = 0.4$, 0.7, 0.8, or 0.9. The most crystalline BN is produced at $x = 0.7$ or 0.8. A 2-mmol reaction with $x = 0.8$ produced a less crystalline BN product with a 73% chemical yield. [e] Unit cells: h-BN, $a = 2.504(1)$ Å and $c = 6.670(1)$ Å; r-BN, $a = 2.50(1)$ Å and $c = 10.01(1)$ Å. [f] Unit cells ($x = 0.8$): h-BN, $a = 2.504(1)$ Å and $c = 6.671(1)$ Å; r-BN, $a = 2.51(1)$ Å and $c = 10.05(1)$ Å.

The crystallinity and yield of the BN products depend on the reaction scale and the precursors used. Generally, larger scale reactions lead to improved crystallinity and higher yields. The less stable boron precursor, $LiBF_4$,[13] gives better crystallinity, but lower yields than its more stable counterparts, $NaBF_4$ and

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(11) (a) The starting materials, $LiBF_4$ (Aldrich, 98%), $NaBF_4$ (Johnson Matthey, 95%), $KBF_4$ (Aldrich), $Li_3N$ (Cerac, 99.5%), and $NaN_3$ (Alfa, 99%), were used as received. Reactions were carried out in a He-filled dry box with screw top stainless steel reactors as previously described.[2] Unless otherwise specified, the data reported is from the washed central portion which accounts for most of the yield. As a typical example of a 20-mmol reaction, 2.1958 g of $NaBF_4$, 0.4875 g of $Li_3N$, and 1.1718 g of $NaN_3$ were ground, pressed into a pellet, and ignited in a reactor. After byproduct fluorides were removed by washing with copious amounts of water (1–2 days stirring required), the recovered products weighed 0.4143 g (theor 0.4940 g). *Caution*! All reactions described are strongly exothermic. Fine $Li_3N$ powders react rapidly with moisture, and $NaN_3$ undergoes thermal decomposition on heating. Very high pressures may build up during reactions when $NaN_3$ is used. (b) Mikroanalytisches Labor Pascher, An der Pulvermuler, D-53424 Remagen-Bendorf, Germany. (c) Temperature measurements were performed in a large chamber equipped with a quartz window under 10 atm of He.

(12) XRD was performed on a Crystal Logic powder diffractometer with graphite-monochromated Cu K$\alpha$ radiation. Scans were carried out in steps of 0.03° in $2\theta$ (or 0.02° with W as an internal standard) at a rate of 5 s/step. SEM and EDS were performed on a Cambridge Stereoscope 250 SEM using gold-coated samples. Infrared spectra were obtained with a Perkin Elmer 1600 FTIR. Density was measured by a flotation method using a combination of $CHCl_3$ and $C_2H_2Br_4$.

(13) Kinetic decomposition temperatures: $LiBF_4$ 200 °C[14] < $NaN_3$ 275 °C[14b] < $NaBF_4$ 406 °C[14] < $KBF_4$ 530 °C[14] < $Li_3N$ melts at 813 °C[14c] and decomposes to Li and $N_2$ at 970 °C.[6b]

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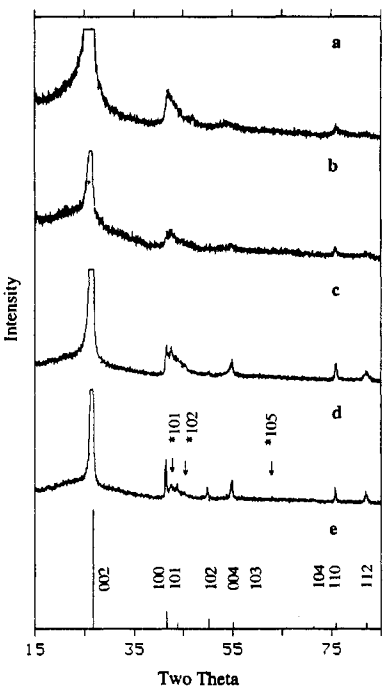

**Figure 1.** Effect of precursors on the crystallinity of BN formed in 20-mmol reactions of (a) $NaBF_4 + 3NaN_3$, (b) $NaBF_4 + Li_3N$, (c) $NaBF_4 + 0.8Li_3N + 0.6NaN_3$, (d) $LiBF_4 + 0.8Li_3N + 0.6NaN_3$, and (e) h-BN standard.[15] **hkl* indicates r-BN as calculated by Rietveld analysis.[16b] The strongest reflection (h-BN (002) and r-BN (300)) at ~26.7° has been truncated for clarity. The amorphous background, which appears significant due to the truncation, is <4% of the strongest peak in part d and is consistent with the high density of the BN products (see text).

$KBF_4$. The reaction of $NaBF_4$ with $NaN_3$ (Figure 1a) or $Li_3N$ (Figure 1b) produces products with XRD patterns characteristic of t-BN,[9,10a] with the latter being more crystalline. The combination of these two nitriding reagents ($0.8Li_3N + 0.6NaN_3$) gives significantly better crystallinity (Figure 1c) than their use individually. Along with the sharpening of all peaks, the broad diffraction hump around 42° in parts a and b of Figure 1 resolves into several peaks in part c, indicative of h-BN[15] and r-BN (ratio: 0.24/0.76).[16] When $LiBF_4$ is used as the boron precursor, even sharper XRD peaks appear (Figure 1d). Along with an increase of the h/r phase ratio to 0.55/0.45, the (100) and (101) peaks of h-BN are now completely resolved. The (102) peak, which is barely evident in Figure 1c, also becomes more pronounced. These changes indicate that the h-modification has increased 3-dimensional order.[9] The average crystallite size estimated using the Scherrer equation[10c,17] is 1150 and 320 Å in the *a*- and *c*-crystallographic directions, respectively. The lattice constants of the BN products (Table 1, footnotes) agree well with literature values for h-BN[15] and r-BN.[16d] The washed boron nitride contains platelets with sizes in the submicron to micron range as revealed by scanning electron microscopy.[12]

Further characterization including density measurements and chemical analysis were used to examine the BN products.[12] The flotation density of the highly crystalline BN produced in reaction 7 ranges from 2.2 to 2.3 g/cm$^3$, comparable with the X-ray density of 2.270–2.272 g/cm$^3$ (from the present and reported lattice parameters of h- and r-BN considering the h/r phase ratio). Using an average density of 2.22 g/cm$^3$, an amorphous BN density of 1.7 g/cm$^3$,[10c] and chemical analysis results (see below) leads to an amorphous fraction of less 7%. The BN product from reaction 8 is about 3% less dense than that from reaction 7. All infrared spectra show two peaks centered at 820 and 1390 cm$^{-1}$ typical of h-BN.[10a,c] No BOH stretches are observed around 3200 cm$^{-1}$. The composition and purity found using physical methods are supported by elemental analysis[11b] of the BN produced from reaction 7: B, 43.2(3); N, 52.5(5); Na, 0.07(0); F, <0.1; Li, 0.12(0); C, 0.22, O, 1.48(4) (corresponding to $BN_{0.94}Na_{0.0007}Li_{0.004}C_{0.005}O_{0.02}$).

The very rapid formation of crystalline BN in the present synthetic approach correlates with the high temperatures, molten fluxes and high nitrogen pressures generated by the carefully selected, highly exothermic routes (see Table 1). Optical pyrometry indicates that reaction temperatures are above 1000 °C.[11c] Theoretically calculated constant-pressure $T_{ad}$ (Table 1) for these reactions are close or equal to the boiling points of the byproduct salts (bp: LiF, 1681 °C; NaF, 1710 °C; KF, 1610 °C).[18] The decreasing crystallinity observed in the $MBF_4 + Li_3N$ reaction series is consistent with their decreasing exothermicities. Note that constant-volume assumptions generally result in even higher $T_{ad}$'s (Table 1) and very high nitrogen pressures when $NaN_3$ is used; e.g., a 20-mmol $NaBF_4 + 3NaN_3$ reaction in our present reactor produces nearly 350 atm and approaches 8500 atm if the reactor is completely filled with the precursors.

Experimentally, the BN product yield, homogeneity, and crystallinity are usually improved with increasing reaction scale. For example, for $NaBF_4 + 3NaN_3$, the chemical yield increases from 45% on a 2-mmol scale to 70% on a 20-mmol scale. This is likely a result of decreased energy losses due to a more efficiently insulated reaction core in larger scale syntheses in our reactor. Further improvements of product yield and quality with even larger scale reactions in sealed high-pressure reactors are expected.

The propagation of these reactions likely involves decomposition of the precursors because the reaction temperatures are significantly higher than the decomposition temperatures of these starting materials.[13] The decomposition of $MBF_4$ produces a gaseous Lewis acid, $BF_3$, thus reducing chemical and diffusion barriers for its reaction with the Lewis base $Li_3N$. The $BF_3$ reactivity is "tunable" since boron precursors of increasing decomposition temperatures can generate $BF_3(g)$ with increasing average energy.

We note that cubic BN, the hardest material known after diamond, can be prepared from r-BN with a facile diffusionless mechanism[16d] and from h-BN under conditions, which, except for pressures of 40 000–60 000 atm, are similar to the present synthesis (1400–1700 °C with alkali fluoride or lithium nitride catalysts).[7,20] Therefore experiments combining the present synthesis with applied high pressures are now in progress.

**Acknowledgment.** We gratefully acknowledge Prof. W. A. Dollase for help with Rietveld refinements and Prof. Z. Munir and Mr. K. Ewald for assistance with temperature measurements. This work was supported by the National Science Foundation and a Dreyfus Teacher-Scholar Award.

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